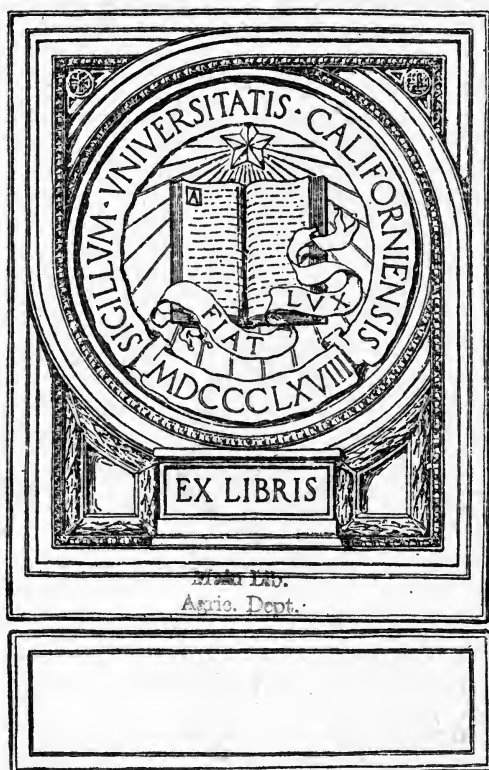


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# United States Department of Agriculture,

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H. W. WILEY, Chief of Bureau.

## COLORING MATTERS FOR FOODSTUFFS AND METHODS FOR THEIR DETECTION.

[A preliminary report made to the Association of Official Agricultural Chemists.]

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### INTRODUCTION.

This preliminary report, including a classification of the colors used in food products and methods for their detection, is published in its present tentative form for the purpose of crystallizing what work has been accomplished in this large field and presenting it for suggestion and criticism. A basis for future work of a more detailed nature is thus afforded, and it is hoped that criticisms and contributions to the subject will be made by those working in this field.

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Approved:

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WASHINGTON, D. C., August 22, 1905.

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### SCOPE OF THE INVESTIGATION.

The field of color chemistry is very large, and the chemist in general analytical practice often neglects it owing to the vast amount of time and patience required for an intelligent understanding of the subject. Much good work has been done toward establishing methods for the recognition of coloring matters in food stuffs, but with the data at present available for such work the individual operator will find himself called upon to exercise his own judgment and apply his own experience to the subject-matter in hand.

The introduction of coal-tar dyes into the field of food stuffs complicates enormously the scope of the work to be covered in an examination of artificial coloring. Were it possible to limit the examination to a certain number of colors, the work would be materially simplified, but no sooner has the analyst perfected color schemes and tabulated reactions for the identification of such colors when new ones are found, rendering previous schemes to a certain extent unreliable and necessarily subject to alteration.

Hence the most that can be hoped for is to establish general methods for determining whether artificial coloring has been resorted to, and, if so, whether the coloring matter is of mineral, vegetable, or coal-tar origin. This fact having been established, special methods must be applied for the separation and identification of the individual coloring matters, often complicated by the presence of mixtures of several coal-tar colors, rendering color reactions useless until each of the separate colors has been isolated.

The food chemist may be called upon for an examination of the coloring matters and commercial preparations used for coloring foods, and for the examination of foods for the presence of artificial colorings, identification of the added color, and the presence of poisonous metals due to the latter. He may also be called upon for an opinion as to the toxic or nontoxic character of the coloring matter, which not only requires an examination for poisonous metals present, as lakes and pigments, but in addition the determination of the presence of poisonous metals due to impurities, the identification of the color or colors, and a knowledge of the toxic effects of the pure color per se.

An examination, therefore, of the colors and preparations employed involves the identification of the heavy metals present, the nature of the color entering into the lake, whether vegetable or of coal-tar

origin, its identification, and, in the case of mixed colors, their separation and identification, and, lastly, the presence of poisonous metals as impurities in the coal-tar dyes, or their presence as inherent constituents of the colors themselves.

Many of the colors contain metallic constituents, as in the triphenylmethane derivatives, especially the greens, such as malachite green, iodine green, ethyl green, victoria green, etc., which contain a double chlorid of zinc in combination with the organic matter. Some of the acridines and thiazines also contain zinc, and naphthol green B contains iron.

In the preparation of the coal-tar dyes many become contaminated with arsenic, copper, zinc, tin, lead, etc., from the use of these metals and their salts during the process of manufacture. Sulphuric acid being used in some stage of the process of manufacture of nearly all the dyes introduces the danger of arsenic being present. Hence all dyes used for artificial coloring which in themselves are harmless may become injurious from the presence of these poisonous ingredients, unless highly purified.

While alum lakes of the vegetable colors are in general harmless, the presence of lakes of tin, antimony, etc., should be carefully guarded against.

The vegetable colors should be examined for the presence of coal-tar dyes of a dangerous nature, and for other vegetable colors and substances and inert mineral matter added for cheapening.

The examination of the food stuffs themselves necessitates determining whether the coloring is due to natural or artificial means, and, if the latter, the color or colors must be separated and an examination of the material made for heavy metals.

In regard to the toxic effects of the purified coal-tar dyes, the chemist must rely upon the experiments and conclusions of investigators in this line of work, and should hesitate to express an opinion on a new color without a physiological test upon living organisms. The experiments of König, Weyl, and others should be consulted on this subject.<sup>a</sup>

Frenzel<sup>b</sup> found that mandarin (sulphanilic acid azo-B-naphthol) and metanil yellow (m. benzene sulpho acid, azo-diphenylamin) could scarcely be considered poisonous in the small quantities in which they are used in foods, but long-continued, large doses give rise to some injurious effects.

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<sup>a</sup> Hygiene of Coal-tar Colors, Koster, Heidelberg, 1882; Poisonous Metals in Dyes, Ashwell and Forth, J. Soc. Chem. Ind., 5, 226, 301; Theerfarben mit besonderer Rücksicht auf Schädlichkeit u. s. w., Dr. Thos. Wehl, 1889; The Sanitary Relations of the Coal-tar Colors, by T. Wehl, Philadelphia, 1892; Effects of Coal-tar Colors on Digestion, Amer. Chem. J., 8, 1092; Conn. Agr. Expr. Stat. Rept., Winton, 1901, p. 179.

<sup>b</sup> Zts. Nahr. Genussm., 1901, 968-974.



Winogradow<sup>a</sup> ascertained that the following dyes hindered the digestion of albumen by pepsin, even when only a few milligrams of the colors were present (an amount corresponding to from one-tenth to one one-hundredth of the digestive solution), this action being almost inhibitive:

Safranin.	Ceruleine S.	Magdala red.
Ponceau RR.	Phloxin RBN.	Azoflavin.
Azofuchsin G.	Iodoeosin.	Benzopurpurin.
Orange II.	Chrysanilin.	Cerise.

The following interfered less than the first-mentioned dyes, but in every case some effect was noticed:

Acid green.	Anilin green.	Martius yellow.
Iodin green.	Primulin.	Metanil yellow.
Acid azo yellow.	Auramin O.	Quinolin yellow.
Yellow T.	Anilin orange.	Methylene green.
Naphthol yellow.		

The methods of separating the colors from the material to be examined by the use of solvents involve the separation of the natural colors at the same time, and these must first be isolated before identification tests can be applied. This fact naturally necessitates a very comprehensive knowledge of the color reactions and the behavior of the natural colors with reagents. Complete data on this subject are as yet wanting.

The coal-tar dyes may, in general, be most satisfactorily separated by the double-dyeing method, with or without previous extraction with solvents, as the case may be, and in some cases may be identified directly by tests on the dyed fabrics, or more accurately by being removed from the fabric and subjected to purification. Great care and judgment must be exercised in applying the color reactions and arriving at a conclusion therefrom, as the presence of more than one dye, or some organic impurity, will lead to erroneous results. Several means of identification should be tried and a conclusion drawn only when the analyst is perfectly satisfied of the identity of the dye.

Many of the results obtained in the determination of a dye have been rendered ambiguous, owing to confusion of names applied to the same dye, and the analyst should always make a point of identifying any particular dye by giving the name of the original manufacturers, so that its composition may be known; as, for instance, orange G might be either of the following in default of a distinguishing mark, viz:<sup>b</sup>

- Orange G (C. J.). Anilin azo  $\beta$  naphthol.
- Orange G (B.). Anilin azo 2 naphthol, 6.8 disulphoacid sodium salt.
- Orange G (H.). Sulphanilic acid azo  $\beta$  naphthol sodium salt.

<sup>a</sup> Zts. Nahr. Genussm., 1903, 589.

<sup>b</sup> Rawson, Gardner, and Laycock, Dictionary of Dyes, Mordants, etc., 1890; Schultz and Julius, Tables of Dyes.

For convenience the finally completed subject might be treated in a systematic arrangement under the following headings, viz:

- I. Remarks in general on coloring matters liable to be present in food stuffs.
- II. Colors to be considered.
  - (1) Coal-tar colors, with their composition, commercial designations, and synonyms.
  - (2) Vegetable colors, their botanical origin, common names, etc.
  - (3) Mineral colors and pigments.
  - (4) Organic lakes.
- III. Harmless and harmful colors and dyes, so far as known.
- IV. Commercial coloring compounds.
- V. Grouping of food stuffs into general classes for examination, as follows:
  - (1) Butter, oils, milk, cheese, etc.
  - (2) Flesh foods.
  - (3) Canned vegetables.
  - (4) Starch foods (noodles, macaroni, etc.).
  - (5) Vinegar.
  - (6) Confectionery.
  - (7) Wines and spirituous liquors, fruit sirups, etc.
  - (8) Brandy, liqueurs, etc.
  - (9) Beer, malt liquors, etc.
  - (10) Tea, coffee, spices, etc.
  - (11) Medicinal preparations.
  - (12) Cosmetics, soaps, etc.
  - (13) Miscellaneous material (tags, paper linings, etc.).

Each class may be treated under the following heads:

- (a) Natural or artificial coloring.
  - (b) Mineral or organic coloring.
  - (c) General methods in detail for detecting the organic coloring matter, and, if possible, isolation of same for identification by tabular schemes.
  - (d) Special tests for colors.
- VI. Each of the thirteen classes in detail, under heads as given under V.
  - VII. Original work on behavior of coloring matters, with solvents and reagents.
  - VIII. Tabular schemes for the identification of the isolated coloring matters.
  - IX. Addenda (what colors allowed, laws, etc.).

It is suggested that the members of the association and collaborators interested in the subject of colors be invited to do what original work their time will permit, on the points suggested below, and communicate their results to the associate referee from time to time as opportunity permits.

(1) Solubility of the coal-tar and vegetable dyes in various solvents (ether, acetic ether, petroleum ether, methyl and ethyl alcohols, acetone, etc.), arranged according to their solubility—as, easily soluble, difficultly soluble, and insoluble.

(2) Extractive values of the various solvents for dyes in neutral, acid, and alkaline solutions.

(3) Characteristics of the coloring matters as contained in fresh fruits, vegetables, wines, etc., with reagents and solvents, with their respective dyeing properties.

(4) Testing such new schemes as may appear in the various current chemical journals, and such as have appeared during the last few years.

This synopsis, together with the classification of colors and the methods of analysis which follow, is intended as an outline for the examination of food stuffs for colors, to be elaborated during the progress of the work.

### CLASSIFICATION OF COLORS.

As a guide to the food analyst, a compilation is given of the vegetable and animal colors, lakes and pigments, which he may be called upon to examine either as to composition and origin or as to suitability for food colors. Many of the old vegetable colors have, of course, been discarded for the coal-tar dyes now employed, which are also classified.

#### I. Coal-Tar Color Lakes. <sup>a</sup>

1. The principal materials used in the preparation of lakes from acid dyes are:
  - Barium chlorid.
  - Lead nitrate and acetate.
  - Zinc sulphate.
  - Aluminum sulphate and acetate and potash, sodium and ammonium alums.
  - Tin chlorid.
  - Antimony chlorid, tartar emetic, double flourids of antimony and sodium or potassium.
  - Calcium nitrate and acetate.
2. Those from basic dyes are:
  - Tannic acid.
  - Phosphate of soda.
  - Sodium arsenite.
  - Stannic and stannous acids and salts.
  - Antimony acids.
  - Resinic and various fatty acids.
3. Principal bases used to modify the color and physical properties of lakes are:
  - Barium sulphate (barytes, blanc fixe, heavy spar).
  - China clay (kaolin).
  - Calcium sulphate (Paris white, satin white, gypsum).
  - Kieselguhr (infusorial earth).
  - Red lead.
  - Zinc oxid.
  - Lead sulphate.
  - Aluminum hydrate.
  - Aluminum arsenite.
  - Barium phosphate.
  - Lead carbonate.
  - Calcium phosphate.
  - Lampblack and vegetable black.
  - Green earth.
4. Colors used may be classed under:
  - (1) Acid triphenylmethane colors.
  - (2) Basic triphenylmethane colors.
  - (3) Azo colors.
  - (4) Oxyketone colors.
  - (5) Azin colors.

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<sup>a</sup> Jennison, Manufacture of Lake Pigments, 1900.

## A. RED LAKES.

Magenta and magenta reds.

Rhodamin B, G, S, 6G, 12G.—Bluish red to reddish pink.

Safranins.

Ponceau 4GBL.—Yellow.

Ponceau GL, GR.—Medium yellow.

Ponceau 4R.—Blue.

Scarlet 3R.—Blue.

Fast red O.—Deep blue.

Reds and maroons from the last four mixed.

Eosins, phloxins, rose bengal—vermillionettes, alizarins—red, scarlet, brown, maroon.

## B. ORANGE LAKES.

Mandarin R, G.—Brilliant orange  
RG.

Orange II. O, R.—Ponceau 4GBL.

## C. YELLOW LAKES.

Auramin.

Metanil yellow.

Thioflavin T.

Quinolin yellow.

Naphthol yellow S.

Tartrazin.

## D. BROWN LAKES.

Bismarck brown.

Acid brown B.

## E. GREEN LAKES.

Acid green D.

Diamond green.

Ethyl green.

Coeruleine.

## F. BLUE LAKES.

Nile blue A.

Diphenylamin blue.

Victoria blue.

Patent blue BN.

Naphthalin blue.

Erioglaucin blues.

Methylene blue B.

Basle blue.

Alkali blue D.

New blue.

Neutral blue.

Water blue.

## G. VIOLET LAKES.

Methyl violet B.

Gallein.

Rhodamins.

## H. BLACK LAKE.

Acid black FHA.

## II. Natural Colors of Vegetable and Animal Origin.

The following list has been compiled from various sources and, as far as possible, verified by consulting botanical literature and by free reference to Dr. Hans Rupe's "Die Chemie der natürlichen Farbstoffe" (Braunschweig, 1900):

Alder bark: Source—*Alnus glutinosa*. Yellow.

Alkanet: Source—*Baphorhiza tinctoria* (*Alkanna tinctoria* Tausch.; *Anchusa tinctoria* L.). Used in coloring medicines, oils, pomades, wine, etc., red to crimson.

Alkanna green has also been prepared from the root.<sup>a</sup>

<sup>a</sup> J. Soc. Chem. Ind., 1903, 512.

- Aloes: Source—Cape aloe, *Aloe spicata*; *A. arborescens*; *A. lucida*; *A. succotrina*; *A. vera*. Yellow.
- Al root; or Aich root, sooranjee (India), suranjee (India): Source—*Morinda citrifolia*; *M. tinctoria*. Alumina lake, yellow.
- Annatto; or anotto, orlean, roucou, orenetto, attalo, terra orellana, achiote: Source—*Bixa orellana*. Used for coloring oils, butter, etc.
- Archil; or orchil, orseille, oricello, orchilla: Source—*Rocella montagnei* (new); *R. fuciformis* (old); *R. tinctoria*. Also prepared from any lichens containing orcin or its derivatives, i. e., variolaria, lecanoria, evernia, cladonia, ramalina, usnea. Appears in liquid, paste, and powder, the latter form being a sulphonated derivative. Dyes unmordanted wool in neutral, alkaline, and acid solutions, and should not be mistaken for coal-tar dyes, in the double dyeing test.
- Asbarg; or gandhaki (Afghanistan): Source—*Delphinium zaili*. Yellow lakes prepared from the blossoms.
- Bahia wood: Source—*Caesalpinia brasiliensis*. Exported from Bahia. Sometimes called Brazil wood. See under Redwoods.
- Barberry: Source—*Berberis vulgaris*. Yellow basic dye.
- Barwood; or camwood, kambe wood, bois du cam: Source—*Baphia nitida*. From west coast of Africa and Jamaica. See under Redwoods.
- Bastard hemp: Source—*Datisca cannabina*. Alkaline solutions yellow.
- Bilberry; or whortleberry: Source—*Vaccinium membranaceum*; *V. myrtillus*. Blue to purple.
- Box myrtle; or yangmoe, of China; kaiphal, of India: Source—*Myrica nagi* (*M. sapida* Wall. and *M. integrifolia* Roxb.); *M. rubra*. Alumina lake, brown orange.
- Brazilwood; or fernambourwood, pernambuco wood, fernambuck wood, bois de fernambouc, rothholz: Source—*Guilandina crista*; *Caesalpinia braziliensis*. Chiefly from Brazil and Jamaica. See under Redwoods.
- Brazilettowood; or Jamaica redwood, Bahama redwood: Source—*Balsamea* sp. See under Redwoods.
- Buckthorn: Source—*Rhamnus cathartica*. Purple juice which when treated with alkali becomes green. Used in confectionery as *sap green*.
- Buckwheat: Source—*Fagopyrum fagopyrum*. Yellow color from leaves and stalk.
- Buttercup: Source—*Ranunculus bulbosus* and other species. Yellow.
- Cabbage: Source—*Brassica oleracea*. Contains cauline, probably identical with the cyanin of wine.
- Camwood; or gaban wood, poa-gaban: Source—Closely allied to barwood. From African coast. See under Redwoods.
- Capers: Source—*Capparis spinosa*. Yellow.
- Caramel: Source—From sugar. Brown.
- Carrot: Source—*Daucus carota*. Yellow.
- Catechu: Source—*Acacia catechu*; *Ourouparia gambier*. Brown to red colors. Influenced by oxidation. Contains catechin.
- Celery; or smallage: Source—*Apium graveolens*. Yellow green.
- Chamomile (Ger.); or matricario: Source—*Matricaria chamomilla*. Alumina lake, yellow.
- Chay root; or chè root, cherri vello, sayavee, imbural, turbuli: Source—*Oldenlandia umbellata*. Contains alizarin, purpurin, etc.
- Chelidoine juice: Source—*Chelidonium majus*. Yellow.
- Chica-red; or crajina, carajara: Source—*Arrabidaea chica* (*Bignonia chica* Humb. and Bonpl.). Vermillion red powder insoluble in water, alkaline solutions, orange to red.
- Chinese green; or lokao: Source—*Rhamnus tinctoria*; *R. dahurica*. Only natural green dye other than chlorophyll.

- Chinese yellow: Source—*Gardenia grandiflora*. Other Chinese yellows are Wongskey, Wougshy, Wongschy, Hoang-tchy, Hoang-teng, Hoang-Tschi, Hoang-pe-pi, and Ti-hoang.
- Chrysamic acid: Source—Aloes. Action of nitric acid on aloes. Yellow in alcohol.
- Chlorophyll: Green color of plants.
- Cochineal; or cochenille, coccionella: Source—*Coccus cacti* (dried bodies of the female insect). Contains carminic acid soluble in water with purple color; lakes, red to purple; alum or tin lakes, cochineal carmine or coccerin.
- Cotinin: Preparation from young fustic. Yellow.
- Cranberry; or red bilberry: Source—*Vaccinium vitisidaea* L. Red.
- Cudbear; or cudbeard, perseo: Source—*Lecanora tinctoria*; *Variolaria orcina*. Differs from archil in being in powder form and free from excess of ammonia.
- Cyanin: Coloring matter from petals of flowers. Occurs in wine. Blue, turning pink with vegetable acids.
- Dragon's blood (palm): Source—*Daemonorops draco*. Red resin.
- Dragon's blood (Socotra): Source—*Dracaena cinnabari*. Red resin.
- Dwarf elder: Source—*Sambucus ebulus*. Red.
- Dyer's broom: Source—*Genista tinctoria*. Yellow.
- Dyer's woodruff: Source—*Asperula tinctoria*. Contains colors similar to alizarin.
- Elderberry: Source—*Sambucus canadensis*; *S. nigra*; *S. pubens*. Red.
- Fairy cup; or blood cup: Source—*Chlorosplenium aeruginosum*. Calcium lake, green.
- Flavin: Prepared from oak bark. Olive yellow to dark brown powder.
- Forget-me-not: Source—*Myosotis palustris*. See Cyanin.
- French purple: Prepared from archil by treatment with acid.
- Fustic (old); or yellow Brazil wood, Holland yellow wood, murier des teinturiers, bois jaune, Gelbholz: Source—*Chlorophora tinctoria* (*Morus tinctoria* L.; *Maclura tinctoria* D. Don.) Contains morin and maclurin. Yellow.
- Fustic (young); or bois jaune de Hongrie, du Tirol, Fisetholz, fustel: Source—*Cotinus cotinus* (*Rhus cotinus* L.). Contains fisitin. Yellow.
- Galangal (Javan): Source—*Alpinia galanga*. Alkaline solutions yellow.
- Galangal (Chinese): Source—*Alpinia officinarum*. Alkaline solutions yellow. Used in Russia for making "Nastoika," a liquor.
- Gamboge: Source—*Garcinia hanburyi*; *G. morella*. Red resin. Lakes, yellow.
- Garancin: Formerly prepared from madder. Of historical interest only.
- Gentian: Source—*Gentiana lutea*. Alkaline solutions yellow.
- Goa powder: Source—*Vouacapoua araroba* (*Andira araroba*) Aguiar. Contains chrysarobin and chrysophanic acid. Yellow.
- Golden seal; or Canadian yellow root: Source—*Hydrastis canadensis*. Yellow basic dye.
- Harmala red: Source—*Peganum harmala*. Basic color insoluble in water; alkaline solutions red.
- Heartsease; or pansy, lady's delight: Source—*Viola tricolor arvensis*. Yields quercetin. Yellow.
- Hollyhock: Source—*Althaea rosea*; *Malva sylvestris*; *M. rotundifolia*. Solutions, violet red. Crimson with acids. Green with alkalis. Alumina lake, violet blue.
- Horse chestnut: Lakes, yellow.
- Indian yellow; or piuri, pioury, purree, purrea arabica, jaune indien. Prepared in India from the urine of cows fed on mango leaves and contains yellow coloring matters, free and in form of magnesium or calcium salts.
- Indigo: Source—*Indigofera anil* and other varieties. Insoluble in water. Becomes soluble by treatment with sulphuric acid, forming sulpho salts. Indigo carmine (blue).
- Jackwood; or jack fruit of Ceylon: Source—*Artocarpus integrifolia*. Alumina lake, yellow.

- Kamala; or kameela, ramelas, rottlera: Source—*Echinus philippensis* (*Rottlera tinctoria* Roxb). Red powder.
- Kermes berries; or portugal berries, poke berries, pigeon berries, scoke berries: Source—*Phytolacca americana* (*Phytolacca decandra* L.). Reddish.
- Kermes; or false kermes berries, grains de kermes, vermilion vegetal: Source—*Coccus ilicis* (dried bodies of the female insect). Solutions and lakes, blood red.
- Kino: Source—*Pterocarpus marsupium*; *Butea frondosa*, *B. superba*, and varieties; *Eucalyptus corymbosa*. Red color.
- Lac-dye; or lac-lac: Source—*Coccus lacca* (from the female insect). Colors similar to cochineal.
- Lapacho; or taigu wood: Source—*Tecoma lapacho* and allied species. Yellow color.
- Lima wood; or Costa Rica redwood: Similar to St. Martha wood. See under Redwoods.
- Liquorice: Source—*Glycyrrhiza glabra*. Brown.
- Litmus; or tournesol: Source—*Rocella*, *Lecanora*, *Variolaria*. Red and blue.
- Logwood; or Campechy wood, Blauholz: Source—*Haematoxylum campechianum*. The unfermented extract forms yellow solutions if neutral, and blood-red solutions with calcareous water. The unfermented solution contains chiefly a glucoside which upon fermentation yields hæmatoxylin, and the latter is easily oxidized to hæmatein. Various colored lakes are formed. Hæmatoxylin forms rose-red color with alum and a black violet lake with iron alum. Hæmatein forms bluish violet with alkalies; reddish purple with sodium carbonate; reddish purple with ammonia; bluish violet lake with ammoniacal copper sulphate; violet lake with ammoniacal tin chlorid; black with ammoniacal iron alum.
- Lopez root: Source—*Toddalia aculeata*. Contains berberin. Yellow.
- Lomatiol: Source—*Tricondylus ilicifolia*; *Tricondylus myricoides*. Yellow.
- Madder: Source—*Rubia tinctorum*. Natural source of alizarin dyes.
- Mang-koudur; or oungekoudon, song-kou-long, jong koutong: Source—*Morinda umbellata*. Lakes, yellow to red.
- Marsh marigold: Source—*Caltha palustris*. Yellow.
- Mountain wormwood; or Genepi des alpes: Source—*Artemisia absinthium*. Yellowish.
- Munjeet: Source—*Rubia cordifolia*. Similar to madder.
- Myrtle berry: Source—*Myrtus communis*. Bluish red.
- Nettle: Source—*Urtica* sp.
- Nicaragua wood: Source—*Guilandina echinata*. Boughs or twigs used. See Redwoods.
- Onion: Source—*Allium cepa*. Alumina lake, yellow brown.
- Oregon grape root: Source—*Berberis aquifolium*. Yellow basic dye.
- Panama crimson: Source—Vine called China.
- Parsley: Source—*Apium petroselinum*. Alumina lake, yellow.
- Peachwood; or St. Martha wood, Martin wood, bois du sang: Source—*Guilandina echinata*. From the Sierra Nevada in Mexico. See under Redwoods.
- Persian berries; or yellow berries, Kreutzbeeren, Avignon-Körner, granes de perse, graines jaune, graines d'Avignon (*Rhamnus infectoria*), French berries (*R. alaternia*), Spanish berries (*R. saxatilis*), Italian berries (*R. infectoria*), Hungarian berries (*R. cathartica*): Source—Species of *Rhamnus* as given above. Alum lake, bright yellow; iron lake, dark olive.
- Poppy; or field red corn: Source—*Papaver rhoeas*. Red.
- Poplar buds: Source—*Populus* sp. Alumina lake, yellow.
- Prickly pear: Source—*Opuntia opuntia*. Red.
- Privet berries: Source—*Ligustrum vulgare*. Bluish red.
- Purple heart: Source—*Copaiva pubiflora*. Alum lake, yellow.

- Puriri: Source—*Vitex littoralis*. Alum lake, yellow.
- Quercitron: Source—*Quercus velutina* and varieties. Yields quercetin, yellow.
- Quebracho: Source—*Quebrachia lorentzii*. Yellow color.
- Redwoods: See Brazil, Bahia, Peach, Nicaragua, Sapan, Lima, Braziletto, Bar, and Camwood. These woods yield on treatment various red to yellow-red colored solutions, no two woods giving exactly the same shades, i. e., Brazilin, probably occurring as a glucoside, forms Brazilin on oxidation and yields lakes similar to alizarine. Florence, Berlin, and Venetian lakes are lakes of the soluble redwoods.
- Rhubarb: Source—*Rheum officinale*. Yields chrysophanic acid, yellow.
- Rue: Source—*Ruta graveolens*. Alum lake, yellow.
- Safflower; or dyer's saffron, carthame, safran bâtard, bastard saffron: Source—*Carthamus tinctorius*. Yellow color. Triturated with French chalk and dried, forms various bright red "rouges."
- Saffron; or azafran (Afgh.): Source—*Crocus sativus*. Yellow.
- Sage: Source—*Salvia officinalis*. Yellow.
- Sandalwood; or santalwood, lignum santalum, red santalwood, Saunders wood, red sandalwood, red Sanders wood, bois de santal, Sandelholz: Source—*Pterocarpus santalinus*; *P. indicus*. Contains santalin, a fine red powder easily soluble in alcohol and acetic acid with a blood-red color. See under Redwoods.
- Sapan wood; or sappan wood, Japan wood, bois du Japon, also called red sandalwood, santalwood, sumbawa wood: Source—*Caesalpinia sapan*. Probably identical with caliatu wood or cariatu wood. See under Redwoods.
- Saw-wort: Source—*Serratula tinctoria*. Alum lake, yellow.
- Sepia: Source—*Sepia officinalis*. Dark-brown ink-like pigment.
- Sorgo red; or durra: Source—*Andropogon sorghum*. Lakes, crimson red.
- Spanish trefoil: Source—*Trifolium* sp.
- Spinach: Source—*Spinacia oleracea*. Yellow.
- Stringy bark: Source—*Eucalyptus macrorhyncha*. Orange to yellow.
- Sun dew: Source—*Drosera whittakeri*. Lakes red to brown.
- Sumac (Cape); or pruin bast: Source—*Colpoon compressum*. Alum lake, yellow.
- Sumac (Sicilian): Source—*Rhus coriaria*. Alum lake, olive yellow.
- Tyrian purple: Source—*Murex*, *purpura*, *buccinum*, etc. (sea shells).
- Turmeric; or curcuma, Indian saffron, terra merita, souchet, safran d'Inde: Source—*Curcuma longa*; *C. rotunda*. Yellow color.
- Ventilago Madras-patana; or oural patti, pittu, lokandi, kanwait, etc.: Source—*Ventilago madraspatana*. Lakes, blue.
- Virginia creeper: Source—*Parthenocissus quinquefolia*. Red color.
- Waifa; or hoai-hoa, Chinese yellow berries: Source—*Sophora japonica*. Alum lake, yellow.
- Wall flower: Source—*Cheiranthus cheiri*. Yellow lakes prepared from the blossoms.
- Wall lichen: Source—*Parmelia parietina*. Yellow.
- Waras: Source—*Moghania congesta* (*Flemingia congesta* Roxb.). Red resinous powder.
- Weld; or wau, gaude, yellowweed, dyer's rocket: Source—*Reseda luteola*. Alum lake, yellow.
- Whitethorn; or blackthorn: Source—*Crataegus oxyacantha*. Yellow lakes from blossoms.
- Woad; or pastel, waid: Source—*Isatis tinctoria*; *I. lusitanica*. Contains indigo.

A large number of vegetable substances contain coloring matters, but are too numerous to mention and are of little interest commercially as yet. Among these the following may be mentioned, their coloring matters having been to some extent studied.



*Ruta graveolens*, *Robinia pseudacacia*, *Rhodospaera rhodanthema*, *Rumex obtusifolius*, *Arctostaphylos uvaursi*, *Polygonum cuspidatum* (in China Kan-yen or Wu-tzu), yellow; *Aristolelia maqui*, red; *Evodia meliaefolia*, yellow.

### III. Organic Lakes.

#### YELLOW.

Alum lakes from various species of buckthorn (*Rhamnus*), Dutch pink being that from Persian berries and commercial Dutch pink that from mixtures of yellow berries, quercitron, and turmeric. Alum lake from Dyer's weld (*Reseda luteola*). Alum lake of gamboge crude or "prepared" (freed from impurities), alum lakes of quercitron, young and old fustic, barberry, annatto, turmeric, saffron, safflower, purree or Indian yellow, and *Gardenia grandiflora*. Quercitron alone is seldom used.

#### RED.

Ammonia compound of cochineal (carmine). Ammonia and alum lake of cochineal (Munich, Vienna, Paris, or Florentine lake). Soda compound of safflower (saffron carmine). Alum lakes of Lac, and Chica, Brazil, Bahia, St. Martha's, Lima, Sapan, and sandalwoods and alizarin.

#### BLUE.

Alum lake of indigo sulphonic acid (new blue, indigo extract, etc.).

#### GREEN.

Alum lakes of chlorophyll, unripe Persian berries (sap-green, "bladder green"), lokao, and lime compounds of buckthorn (Charvin's green).

#### VIOLET.

Lime compounds of lokao and archil (French purple). Alum lakes of alkanet and logwood.

### IV. Mineral Pigments.<sup>a</sup>

#### YELLOW.<sup>b</sup>

Active ingredients.		Active ingredients.	
Chrome yellow.....	Pb. Cr.	Zinc chrome yellow.....	Zn. Cr.
Cassel yellow.....	} Pb. Cr.	Cadmium chrome yellow.....	Cd. Cr.
Mineral yellow.....		Cadmium yellow.....	Cd. S.
Veronese yellow.....		Mars yellow.....	Fe. Ca. Al.
Montpelier yellow.....	Pb. Cr.	Siderin yellow.....	Fe. Cr.
Turner's yellow.....	} Pb. Cr.	Aureolin yellow.....	Co.
English yellow.....		Turpeth mineral yellow.....	Hg.
Naples yellow.....	Pb. Cr.	Realger yellow.....	As.
Antimony yellow.....	Pb. Sb. Bi.	Orpiment yellow.....	} As.
Calcium chrome yellow.....	Cr. Ca.	King's yellow.....	
Barium yellow.....	} Cr. Ba.	Mosaic gold.....	Sn.
Yellow ultramarine.....			
Permanent yellow.....			

<sup>a</sup> Bersch, Manufacture of Mineral and Lake Pigments, 1901; also consult, in this connection, an official list of prohibited colors in Braunschweig, Zeit. öffent. Chem., 1898, p. 453, and Vereinbarungen . . . Nahrungs-und Genussmitteln für das Deutsche Reich, Berlin, 1897.

<sup>b</sup> Bracketed colors are synonyms.

*RED.*

Vermilion .....	Hg.	Chrome orange .....	} Pb. Cr.
Antimony vermilion....	Sb.	Persian red .....	
Hematite .....	Fe.	Derby red .....	
Vogel's iron red.....	Fe.	Chinese red .....	
Macay's English red....	Fe.	Indian red .....	
Indian red .....	Fe.	Cobalt red .....	Co.
Chrome red.....	} Pb. Cr.	Cobalt magnesium red..	Co. Mg.
Chrome vermilion.....			

*BLUE.*

Persian blue .....	} Fe. CN.	Newberg blue .....	} Cu.
Chinese blue .....		Lime blue .....	
Berlin blue .....		Payen's blue .....	
Paris blue .....		Oil blue.....	Cu.
Brunswick blue .....		Cobalt blue .....	} Co. Al.
Mineral blue .....		Thenard's blue.....	
Turnbull's blue.....	Fe. CN.	King's blue .....	
Antwerp blue .....	Fe. CN.	Leyden blue .....	
Ultramarine .....	Al. SiO <sub>2</sub> .	Cobalt ultramarine .....	
Bremen blue .....	Cu.	Ceruleum .....	Co. Sn.
		Blue ashes .....	Cu.
		Mountain blue .....	Cu.

*GREEN.*

Scheele's green.....	} As. Cu.	Chrome green.....	Cr.
Swedish green .....		Guignet's green .....	Cr.
Brunswick green .....	} As. Cu.	Emerald green .....	Cr.
Green verditer .....		Turkish green.....	Cr.
Neuweid green .....	As. Cu.	Leaf green .....	Cr.
Bremen green .....	Cu.	Arnaud's green .....	Cr.
Emerald green .....	As. Cu.	Plessy's green.....	Cr.
Verdigris .....	Cu.	Schintzer's green .....	Cr.
Mitis green .....	Cu.	Cobalt green .....	Co. Zn.
Kuhlmann's green .....	Cu.	Manganese green.....	} Mn. Ba.
Elsner's green .....	Cu.	Rosenstiehl's green.....	
Casselmann's green.....	Cu.	Böttger's green.....	Mn. Ba.
Lime green .....	Cu. As.	Silk green .....	Pb.
Patent green .....	Cu. As.	Natural green .....	Cr., picric acid.
Egyptian blue green....	Cu.	Nonarsenical green .....	Cu. Cr. Fe.

*VIOLET.*

Chromium chlorid .....	Cr.	Mineral lake .....	Sn. Cr.
Manganese violet.....	} Mn.	Copper violet .....	} Cu.
Nuremburg violet .....		Guyard's violet .....	
Tin violet.....	Sn. Cr.		

*BROWN.*

Lead brown.....	Pb.	Copper brown.....	Cu.
Manganese brown .....	Mn.	Hatchett brown .....	Cu. CN.
Pyrolusite brown .....	Mn.	Chrome brown .....	Cu. Cr.
Prussian brown .....	Fe. CN.	Cobalt brown .....	Co. Fe.
Iron brown .....	Fe.		

A comprehensive list of the commercial names of pigments, with their synonyms in English, French, German, and Latin, will be found on page 460 of Bersch's work on pigments.

## V. Coloring Compounds.

Name.	Use.	Said to contain.
Carottine .....	Butter.....	Solution of 1 part annatto in 4 parts oil.
Orantia .....	Butter.....	Mixture of annatto and sodium carbonate.
Beer color .....	Beer .....	Starch, sugar, $\text{Na}_2\text{CO}_3$ ; soluble in 75 per cent alcohol.
Vinoline .....	Wine .....	Mixture of reds, usually rosanilin salts.
Bordeaux-Verdisant.	Wine .....	Methylene blue, diphenylamin orange, fuchsin S.
Teinte de Fismes....	Wine .....	Elderberry juice, alum.
Teinte Bordelaise ...	Wine .....	Currant sirups, 4 per cent alcohol.
Saffron substitute....	Wine .....	Nitro-cresol, potash salt, 40 per cent sal ammoniac.
Önocyenin.....	Foods .....	Thick liquid; gives reaction for wine color; contains 74 mg. copper <sup>a</sup> per liter.
Sanguis.....	Sausages....	Contains red coal-tar dye similar to ponceau.
Rosalit. ....	Sausages....	Ammoniacal solution of carmine and saffran extract.
Macilin.....	Meat .....	Wheat starch, potato starch, azo dye.
Albo-Carnit.....	Sausages .....	Faintly colored solution of sugar 4.4 per cent, $\text{KNO}_3$ 1.5 per cent, $\text{NaCl}$ , and boric acid.
Rubro-Carnit .....	Sausages....	Coal-tar dye in $\text{H}_2\text{O}$ , 3.5 per cent.
Roseline.....	Sausages....	Carmine.
Brilliant berolina ...	Sausages....	Ponceau 2G.
Blutroth, meat juice.	Meat .....	Ponceau 2R.
Krebsfarbe .....	Meat .....	Orange G.
Wurstroth.....	Sausages....	Eosin.
Darmröthe .....	Sausages....	Orange II or Mandarin G extra, sodium salt of sulphanyl (or toluidin sulpho-acid), azo-B-naphthol.
Krebsfarbe .....	Sausages....	Ponceau RT.
Zanzibar carbon ....	Meat .....	Coal-tar dye similar to Vesuvium or Bismarck brown.
Freeze-Em .....		Dye similar to tropeolin.

## METHODS OF ANALYSIS.

## I. Wines.

The natural coloring matter of red wine is cenolin, similar in its properties to anchusin of alkanet. There is also said to be a blue color present identical with the cyanin of flowers. The varying depths of color in red wines is probably due to the coloring matter contained respectively in the pulps and the skins of the grapes employed, usually to the latter source.

The coloring matter of the pulp is very similar in its properties to that of the black currant, elderberry, and bilberry, making these latter very difficult if not wholly impossible to detect when present in wines. The examination of a wine for artificial coloring may cover the entire range of vegetable colors and include a very long list of the coal-tar colors, although in most cases these colors are confined to a comparatively limited area; a certain class of red coal-tar colors being much more frequently met with, as the usual added coloring matter (when colored at all), i. e., ponceaus, tropæolins, oranges, Biebrich scarlets, etc., belonging to the azo dyes and the safranins of the triphenylmethane series.

## A. PRELIMINARY TESTS.

a. EXAMINATION FOR NATURAL OR ARTIFICIAL COLORING MATTERS. <sup>a</sup>

Reagent.	Reactions for normal wine.	Reactions for suspicious wine.
1. Add ammonia to 20 cc of wine until alkaline, then a few drops more, agitate, pour into glazed porcelain dish.	Greenish blue; green or yellowish green; yellowish with some brown (old wine).	Red brown; garnet; reddish black; reddish green.
2. Add subacetate of lead in slight excess to 20 cc of wine, about 6 cc to 8 cc, agitate and filter.	Precipitate varying from grayish blue to greenish blue or gray; filtrate colorless.	Precipitate deep green, green, red green, or grayish red; filtrate uncolored, or more often colored.
3. Add 5 cc of 10 per cent solution of alum to 10 cc of wine, to which has been added previously a weak solution of potassium carbonate (until the color does not deepen), then add 5 cc of a 10 per cent solution of potassium carbonate. (Neutralization must be assured.)	Lake colored bottle green without blue or violet tint; filtrate uncolored, green, or lilac, in the latter case becoming green on adding sodium carbonate.	Lake is colorless, violet, or rose; filtrate is blue, violet, or rose, and does not turn green on adding potassium carbonate.
4. Add 10 cc of saturated solution (in the cold) of alum to 10 cc of wine, and then, drop by drop, a concentrated solution of neutral acetate of lead until precipitation is complete, and filter.	Filtrate light wine color .....	Filtrate blue, violet, gooseberry blue.
5. Agitate 10 cc of ether and 10 cc of wine in a test tube.	Ethereal layer colorless .....	Ethereal layer yellow or violet. Ammonia added to the ethereal layer gives yellow to red (campechy), violet to deeper violet (archil).
6. Add 10 cc of solution of alum — 2° B. to 10 cc of wine previously brought to a violet tint by addition of potassium carbonate.	Mixture wine-colored lilac, very intense, or garnet.	Mixture violet blue.
7. Small bit of fulminating cotton is placed in a tube with 20 cc of wine and agitated for a minute or two, well washed with distilled water, and dried.	Cotton white or faint wine red, becoming green with ammonia.	Cotton rose, red brown, or blue, disappearing on addition of ammonia and not becoming green.
8. Fifty cc of wine made just alkaline with baryta water, then 25 to 30 cc of neutral amyl alcohol. Agitate several times and allow to settle.	Amyl alcohol colorless, a filtered portion remaining so when acetic acid is added.	Amyl alcohol colored, or becomes colored rose, yellow, or violet with acetic acid.
9. Add 40 centigrams of yellow oxid of mercury finely pulverized to 20 cc of wine, heat to boiling, and filter through double filter paper.	Filtrate colorless, remaining so after adding acid; residue, treated successively with boiling water, alcohol, and amyl alcohol, does not color either solvent.	Filtrate colored, or becoming so when acidified; residue treated in same manner with solvents colors some or all of them.
10. Equal weights of dioxid of manganese natural, pulverized, and wine are agitated for 5 minutes, then filtered.	Filtrate colorless or yellow tinted.	Filtrate rose color.
11. Boil a small piece of flannel, well bleached and washed, with 20 to 30 cc of wine; evaporate to dryness, wash flannel with distilled water, and observe the color; then treat with ammonia.	Wool faintly colored like wine lees; treated with ammonia yellowish green.	Wool colored.

Three preliminary tests are used, and wines are considered genuine as to color if they respond to these tests.

(1) Sticks of chalk are steeped in a 10 per cent solution of egg albumen and dried first in the air and then at 100° C. The wine is tested by allowing two drops to fall on a surface of the chalk from which the excess of albumen has been removed by scraping. Genuine wines give a gray color, and young and highly colored wines may give a somewhat bluish tint, but there should be no trace of green, violet, or rose.

(2) The wine is made alkaline by baryta water until it is of a greenish hue. It is then shaken up with acetic ether or amylic alcohol. If the wine is pure there is no color in the upper layer, with or without the addition of acetic acid. On the other hand, coal-tar colors of a basic nature color the solvent and give indications suggestive of amido-benzene, fuchsin, safranin, etc.

(3) Ten cc of wine are made alkaline until the wine becomes of a green color by the addition of a 5 per cent caustic potash solution. To this are added 2 cc of a solution of mercurous acetate. The whole, after shaking, is filtered. With pure wine the filtrate is colorless, both before and after acidulating with hydrochloric acid, while coal-tar colors of an acid nature tint the filtrate red or yellow.

*Dupré test.<sup>b</sup>*

A jelly is made by dissolving 5 grams of gelatin in 100 cc of warm water and pouring the solution into a square flat mold made of paper. From this cake cubes about three-fourths inch square are cut with a sharp wet knife and are immersed in the wine, taken out after the lapse of from twenty-four to forty-eight hours, washed slightly, and sections cut, in order to see how far the coloring principles have penetrated. If the wine is pure, the color will be confined almost entirely to the edges of the slice, or will not have penetrated beyond one-sixteenth to one-eighth of an inch. Most other coloring matters rapidly permeate and color the jelly.

(1) Colors penetrating slowly:

Coloring matter of pure wine.

Coloring matter of rhatany root.

(2) Colors penetrating rapidly:

Rosanilin. Litmus.

Cochineal. Red cabbage.

Logwood. Beet root.

Brazil wood. Wayside mallow.

Indigo. Marsh mallow.

*b. EXAMINATION FOR COAL-TAR COLORS.*

*Mansfield's test.<sup>c</sup>*

Dilute 25 cc of red wine in two large test tubes to 100 cc with water. Add a few drops of hydrochloric acid to one and a few drops of ammonia to the other and 10 cc of amyl alcohol to both. Agitate without shaking, allow to settle and drain off alcohol from both.

(1) *Alcohol from acid solution.*—The amyl alcohol is colored red. On addition of ammonia (dilute) the color becomes green and passes into the water solution, chang-

<sup>a</sup> Report on processes in use at the municipal laboratory, by Doctor Muter, analyst, 1885.

<sup>b</sup> Blyth, *Foods, etc.*, 5th ed., 1903.

<sup>c</sup> Dr. M. Mansfield, *Zts. Nahr. Genussm.*, 1897, 55.

ing soon to brown. The liquid is red, and after addition of ammonia (dilute) changes to violet blue.

(2) *Alcohol from ammonia solution*.—Amyl alcohol uncolored. On adding water and a few drops of hydrochloric acid no color should develop. The liquid is brown and becomes red on addition of hydrochloric acid.

If the wine gives these reactions, then no coal-tar colors are present.

*Cazeuere's test.*<sup>a</sup>

For the detection of coal-tar dyes containing the sulpho-group (acid fuchsin, etc.), azo colors, Bordeaux red, ponceaus, congo, etc., 0.2 gram of mercuric oxid is added to 10 cc of wine in a test glass and shaken vigorously for about half a minute, heated to boiling, and passed through a double filter paper. If the coal-tar colors are present, the filtrate will be colored red. Wines containing a large amount of tannin sometimes give a light-gray color. Red oxid of mercury can not be used for this purpose. Some very dark genuine red wines<sup>b</sup> (from Trollinger and Portuguese grapes) will give a red filtrate under these conditions.

In most natural red wines, however, under these conditions the red color is destroyed.

*Falieres-Ritter test.*<sup>c</sup>

One hundred cc of wine are made alkaline with 5 cc of ammonia and shaken vigorously with 30 cc of ether in a suitable retainer. With a pipette remove 25 cc of the ethereal layer (filtration is not allowable as the filter paper retains fuchsin) and evaporate in a white porcelain dish with addition of acetic acid and a strand of white wool. After evaporation of the ether the wool will be dyed<sup>d</sup> if coal-tar colors are present and remain white in the absence of such colors.

c. EXAMINATION FOR FOREIGN VEGETABLE COLORS.

No reliable method can at present be given for the detection of the presence of added vegetable colors in general, and recourse must therefore be had to the special tests for vegetable colors given below. The presence of vegetable colors may be assumed if, after proving the absence of coal-tar colors, the wine fails to come up to the tests for pure wines, as given under this heading. In the absence of coal-tar colors, and when by the preceding examination the presence of foreign vegetable colors is indicated, the following procedure will be found useful for indications of the character of the coloring matter present, but in any case the presence and identity of the indicated color should be proved by confirmatory tests to be found in any of the text-books.

Evaporate a sufficient quantity of the wine, depending upon the amount of coloring matter present, to small bulk, then make slightly acid with acetic acid, insert a piece of wool previously mordanted with tin, and evaporate to dryness in a porcelain dish. If the wool is dyed, remove it and wash thoroughly with water, note the color it is dyed, and examine portions of the fiber according to the following table:

<sup>a</sup> Compt. rend., 1886, 102, 52.

<sup>b</sup> Bujard and Baier, Hilfsbuch., p. 295.

<sup>c</sup> Röttger, Lehrbuch der Nahrungs-Chemie, 1903, p. 478.

<sup>d</sup> Fuchsin will be indicated by disappearance of the color on treating the wool with ammonia.

*Reactions of vegetable colors on wool, mordanted with tin salts.*

Colors produced by various reagents.									
Coloring material.	Hydrochloric acid (sp. gr. 1.16).	Sulphuric acid (sp. gr. 1.84).	Nitric acid.	Stannous chloride, hydrochloric acid, and water.	Sodium hydroxide (10 per cent solution).	Boiling alcohol.	Boiling soap (1 per cent solution).	Boiling sodium carbonate (4 per cent solution).	Boiling 5 per cent sulphuric acid solution.
Logwood .....	Red violet.....	Olive-brown; yellow on dilution.	.....	Red to violet.....	Violet.....	No color.....	No color.....	No color.....	Red to orange-red.
Fustic .....	Yellow solution; colorless on dilution.	Solution yellow; on dilution remains yellow.	Brown; on addition of soda, red.	Little action.....	Brown; solution decolorized on adding hydrochloric acid.	No color.....	Solution deeper yellow; fiber straw color.	As with soap.....	Solution yellow; fiber not greatly affected.
Young fustic ..	Solution yellow ..	Fiber orange; solution yellow; colorless on dilution.	Fiber dark brown.	Solution faint yellow.	Yellow.....	.....	.....	.....	.....
Quercitron .....	Yellow solution; colorless on dilution.	Yellow solution; yellow on dilution.	Orange-yellow; red with caustic soda.	Little action.....	Fiber brown; solution yellow.	No color.....	Solution faint yellow; fiber brown; but not much lighter.	Yellow solution; fiber brown-yellow.	Solution yellow; fiber not much affected.
Weld .....	Little affected....	Yellowish olive; on adding water decolorized.	Little affected.	Fiber redder.....	Little affected.	.....	.....	.....	.....
Persian berries.	Not distinctive from weld.	.....	.....	Fiber yellower.	.....	.....	.....	.....	.....
Turmeric.....	Fiber reddish; solution pale pink; on dilution fiber bright yellow.	Fiber and solution reddish-brown; on dilution fiber pale straw; solution colorless.	At first deep red, then yellow.	Bright-reddish orange fiber and solution.	.....	Yellow solution; green fluorescence.	.....	Orange solution; fiber light brown.	Pale-yellow solution; fiber paler; red orange on addition of caustic soda.
Brazil wood...	.....	Fiber brown; solution yellow	.....	Fiber yellow.....	.....	Yellow.....	.....	.....	.....
Campechey wood.	Fiber crimson; liquid colorless.	Fiber and liquid dark maroon.	Brown.....	Bluish red.....	.....	No color.....	.....	Fiber bluish; solution no color.	.....
Orchil and eudbear.	Solution and fiber red.	Fiber and solution purple; solution on dilution red and fiber almost colorless.	Yellow.....	Decolorized.....	Fiber and solution bluish-purple; color slowly removed.	Bluish-red solution.	.....	Violet solution.	Orange solution; turned violet by soda.
Cochineal.....	Orange-red.....	Dark violet.....	Yellow.....	Orange.....	Red-violet.....	No color.....	.....	.....	.....

## B. SEPARATION AND IDENTIFICATION OF THE COAL-TAR COLORS.

### a. METHOD OF SOSTEGNI AND CARPENTIERI.

Zts. anal. Chem., 1896, 35, 397; U. S. Dept. Agr., Div. of Chem., Bul. 46, Rev., p. 68; Bul 65, p. 111 (Tolman).

### b. ARATA'S METHOD.

Zts. anal. Chem., 1889, 28, 639; U. S. Dept. Agr., Div. of Chem., Bul. 65, p. 112 (Tolman).

It must be observed that certain natural coloring matters dye wool in the second bath, i. e., orchil, cudbear, etc. See Tolman, J. Amer. Chem. Soc., 1905, 27, 25.

### c. WOLFF-WINTERTHUR METHOD.

This is an application of the method of Cazeneuve (already described) for the separation of the coloring matters into groups. Proceed as follows:

Ten cc of wine are shaken with a cold saturated solution of mercuric chlorid, and after the addition of 10 drops of potassium hydrate (sp. gr. 1.27) and again shaking, is passed through a dry filter paper.

(1) Faint yellow filtrate: Add acetic acid to acid reaction; the filtrate becomes rose colored. Acid fuchsin.

(2) Filtrate; yellow red, rose, red-violet. Acidify with hydrochloric acid; (a) the color remains unchanged or only rose colored: Oxyazo colors, as Bordeaux, ponceau, etc.; (b) the color changes from yellow-red to blue-red or blue-violet: Amidazo colors, as Congo, benzopurpurin, methyl orange, etc. Excess of alkali brings back the original colors.

### d. DETECTION OF COAL-TAR COLORS BY EXTRACTION WITH SOLVENTS.

#### *Paris municipal laboratory method.*

Girard and Dupré, Anal. de matières, etc., p. 167; U. S. Dept. Agr., Div. of Chem., Bul. 65, p. 113 (Tolman).

As the solubility of the numerous coal-tar colors in amyl alcohol from alkaline and acid solution has not as yet been satisfactorily tabulated, complete reliance can not be placed on the use of amyl alcohol as the sole solvent for all dyes; hence the writer suggests the successive extraction of the solution both in acid and alkaline condition with such solvents as ether, acetic ether, acetone, and benzol, in addition to the amyl alcohol, combining the alkaline extracts and the acid extracts, and evaporating each of the combined extracts separately to dryness, after washing and filtering, in the presence of a piece of wool. The basic and acid colors will then be dyed on separate pieces of wool and can be further examined. In either of the above methods the dyed wool should be further examined for the identity of the coal-tar color or colors. This may be done directly on the dyed fiber<sup>a</sup> to a certain extent, or by dissolving out the dye and applying reagents to the extracted dye.

To remove the color wash the wool with dilute tartaric acid and then with water and dry between filter paper. Saturate the wool with strong sulphuric acid and press out the color with a glass rod after from five to ten minutes and dilute with 10 cc of water. Remove the wool, make solution alkaline with ammonia, and when cold extract with 5 to 10 cc of amyl alcohol or other suitable solvent. Separate the

<sup>a</sup> Lehne and Rusterholze, J. Soc. Chem. Ind., 14, 72; Analyst, 1899, 24, 41.



solvent, evaporate to dryness, and examine the color residue by the schemes given in the following references, consulting the tables of Schultz and Julius.<sup>a</sup>

Witt, *Analyst*, 11, 111.

Allen, *Com. Org. Anal.*, 3, (1), 399-420.

Weingartner, *J. Soc. Dyers*, 3, 67.

Dommergue, *Zts. anal. Chem.*, 1887, 26, 100; *J. Soc. Chem. Ind.*, 8, 216.

Girard, *Zts. anal. Chem.*, 1888, 27, 232.

Dupré, *Zts. anal. Chem.*, 1890, 29, 369.

Girard and Pabst, *Compt. rend.*, 101, 156.

Sorby, *Proc. Royal Soc.* No. 92, 1867.

Schoop, *J. Soc. Dyers*, 2, 7.

Stein, *Dingl. Polyt. J.*, 210, 245.

Goppelsroeder, *J. Soc. Dyers*, 4, 5.

Fol, *J. Chem. Soc.*, 28, 193.

Hummel and Lepetit, *J. Soc. Dyers*, 4, 133.

Leach, *Food Inspection and Analysis*, New York, 1904. A table including about 50 selected coloring matters which are adapted for and have been found in foods by various analysts, as listed in State and Government reports, as well as in laws of various countries dealing with food colors.

Most colors may be conveniently narrowed down to groups and classes by the scheme devised by Rota, given in *Provisional Methods of Food Analysis*.<sup>b</sup>

#### c. SPECIAL TESTS FOR COAL-TAR COLORS.

##### 1. *Determination of acid magenta—Girard's method.*

Girard and Dupré, *Analyse des matières alimentaires*, etc., p. 169; Winton, *Conn. Agr. Expt. Sta. Rept.*, 1899 (2), 132; Tolman, *U. S. Dept. Agr., Div. of Chem.*, *Bul.* 65, p. 114.

##### 2. *Test for Martius yellow or naphthalene yellow.*

Tolman, *loco cit.*

##### 3. *Test for naphthol colors.*<sup>c</sup>

Fifty cc of wine are acidified with a few drops of hydrochloric acid and wool yarn placed in the liquid. Boil one-fourth hour. Wash the wool with water and then boil in fresh water with a few drops of hydrochloric acid for another one-fourth hour. Wash the wool thoroughly with water and warm with fresh water containing a few drops of ammonia to dissolve the dye. The solution becomes red. Acidify the ammoniacal solution with hydrochloric acid and dye another piece of wool. Examine the dyed wool for identity of dye.

##### 4. *Test for Bordeaux red.*<sup>d</sup>

Casali found that the artificial coloring of Italian wines was a very general practice, those from the central provinces being chiefly colored with a "Vinoline" red and those from the south with Bordeaux red (azo-naphthyl-naphthol sulphonic acid). Treat 50-100 cc of wine with 10-20 per cent of a 10 per cent solution of barium chlorid and sufficient potassium bisulphate solution to precipitate the barium introduced. When the precipitate has subsided, decant the supernatant liquid, add 3-6 cc of hydrochloric acid and sufficient water to restore to its original volume, and boil for five to ten minutes with a little fat-free wool. In the presence of Bordeaux red the wool is dyed a bright red color, which does not change on adding ammonia.

<sup>a</sup> *Tabellarische Übersicht der künstlichen organischen Farbstoffe*, 4th ed., Berlin, 1902; revised 2d ed. in English, by A. G. Green.

<sup>b</sup> *U. S. Dept. Agr., Bureau of Chemistry, Bul.* 65, p. 115.

<sup>c</sup> *Fresenius, Anleitung zur chem. Analyse des Weines*, p. 92.

<sup>d</sup> *Staz. Speriment. Agrar. Ital.*, 1900, 33, (2), 183-189.

## C. SPECIAL TESTS FOR VEGETABLE COLORS.

A great many tests for vegetable colors are given, depending largely on color reactions with different reagents, but these must be used with very great discrimination, as they depend very largely on a fine judgment of shades of colors, which many eyes are not able to distinguish.

A great deal of work has been done on detection of vegetable colors,<sup>a</sup> but only in a very few cases are the reactions specific enough to be decisive.

## a. DETECTION OF CARAMEL—ANTHOR TEST.

U. S. Dept. Agr., Div. of Chem., Bul. 65, p. 120; Modification, Bul. 90, p. 226; Zts. anal. Chem., 1885, 24, 30.

## b. DETECTION OF TURMERIC.

U. S. Dept. Agr., Div. of Chem., Bul. 51, p. 131; Bul. 65, p. 120.

c. TEST FOR CHERRY JUICE.<sup>b</sup>

Windisch found that all cherries examined by him contained hydrocyanic acid, as did also the fermented juice with or without the stones. From this fact he proposes the following test:

Distill 20–30 cc of the liquid until 2 cc have been collected, and to this distillate add a drop of guaiacum tincture, together with a drop of copper sulphate solution. A blue color indicates hydrocyanic acid. The color is fugitive, and if very faint may be intensified by shaking out with chloroform in which it is soluble. Unfortunately, however, a negative test does not prove the absence of cherry juice.

d. KERMESE <sup>c</sup> (*Phytolacca*).

Add lead acetate, kermese gives red-violet precipitate; add barium hydrate, kermese gives blue-violet flocks.

## II. Brandy, Rum, Liqueurs, Vinegar, etc.

## GENERAL DISCUSSION.

Coal-tar colors may be examined for in the usual way as under wines, after previously boiling out excess of alcohol and filtering off any coloring matter precipitated. The color of brandy may be due to the presence of caramel or a deepening of the tint by coloring matter due to the cask. Arrack is nearly colorless, but may have a slight tinge of yellow or brown due to long storing in casks. Liqueurs are often brightly colored by vegetable coloring matters such as chlorophyll, turmeric, cochineal, etc. Absinthe is yellowish-green in color,

<sup>a</sup> Girard and Dupré, *Analyse des matières alimentaires*, etc., 580–581, also 169; A. W. Blythe, *Foods, Their Composition and Analysis*, pp. 91–109; Allen, *Commercial Organic Analyses*, 3, (1); E. Brucher, *Falsification des substances alimentaires*, p. 162; W. Lenz, *Zts. anal. Chem.*, 1885, 24, 285.

<sup>b</sup> *Zts. Nahr. Genussm.*, 1901, 817.

<sup>c</sup> Bujard and Baier, *Hilfsbuch*, etc., p. 296.

due to chlorophyll added for this purpose in the form of juice from spinach, parsley, etc. The following colors may be looked for:

Cochineal, saffran, safflor, curcuma, indigo (soluble), litmus, sap-blue, caramel, licorice root, and coal-tar colors (alizarines, Magdala red, primrose, etc.).

Doctor Mansfield<sup>a</sup> proposes to treat spirits and similar liquid in the following way when they contain red coloring matter insoluble in water:

Treat with water and a drop of 5 per cent sodium hydroxid.

Solution contains the alizarine colors.

Residue: Heat with 70 per cent alcohol.

If soluble and fluorescent add 33½ per cent sodium hydroxid solution.

If fluorescence disappears—Magdala red.

If fluorescence remains—Primrose.

Hubert<sup>b</sup> states that the color of genuine absinthe (chlorophyll) is usually derived from *Artemisia pontica*, with the addition in some cases of hyssop. Inferior absinthes contain more or less color derived from artemisia but in addition other coloring principles, such as that of veronica. For the detection of foreign coloring matters he recommends the following procedure:

Shake 20 cc of absinthe with several successive portions (5 cc) of chloroform until no more color is extracted. The extract is evaporated and the residue taken up with water. If the solution is colorless, or has only a faint yellow tint, the absinthe is free from artificial colors.

#### TEST FOR CAMEL (CRAMPTON AND SIMONS).<sup>c</sup>

Fifty cc are measured out at a standard (room) temperature, and evaporated on a water bath nearly to dryness; the residue is washed into a 50 cc glass-stoppered flask, 25 cc absolute alcohol added, and the solution, after cooling to the standard temperature, is made up to the mark with water. After mixing, 25 cc of the solution are transferred to the separatory apparatus shown in fig. 1 and treated with 50 cc of ether for half an hour, being shaken at intervals; at the end of this period, the layers having separated well, the lower layer is made up with water to the original volume, 25 cc. This is conveniently accomplished by connecting the lower end of the apparatus with a rubber siphoning tube which carries water from an elevated flask, the inflow of water being regulated by the stopcock of the apparatus.

The contents of the flask are again shaken, and again allowed to separate (whereby the volume of the lower layer is slightly increased), and the watery layer is drawn off through the stopcock for a reading of its color in the tintometer. At the same time a reading is taken of the 25 cc of the solution which was not subjected to the treatment with ether; from these two readings the amount of color extracted by ether is



FIG. 1.—Separatory apparatus used in test for caramel.

<sup>a</sup>Zts. Nahr. Genussm., 1897, p. 56.

<sup>b</sup>Ann. chim. anal., 1901, 409; Analyst, 1902, 55.

<sup>c</sup>J. Amer. Chem. Soc., 21, 355; 22, 810.

calculated in percentages. The method is based on the fact that caramel is insoluble in ether and that after the treatment with ether the liquid remaining (if colored) can be compared colorimetrically with the original spirits. The authors' original method <sup>a</sup> for separating caramel by means of fuller's earth may be used as a valuable supplementary test.

### III. Malt Liquors.

#### NATURAL AND ARTIFICIAL COLORS.

The natural coloring matter of malt liquors is due to the coloring matter present in the malt and hops used in the preparation of same. The coloring matter of malt has been examined by Sorby and examined spectroscopically. It is an orange yellow color which becomes deeper yellow with ammonia and 50 per cent sulphuric acid. Fermentation modifies somewhat the characteristics of the pure coloring matter. Carbonizing and drying at high heat produces, besides the original yellow color, a brown color, probably caramel or similar color. Lupulin, the coloring matter of hops, is also yellow. The addition of vegetable extracts for the purpose of furnishing added "bitters" may produce more or less artificial brownish yellow shades—i. e., chiretta, quassia, wormwood, gentian, aloes, extractives, etc., containing alkaloids, giving color reactions with various reagents. The subjoined table shows the characteristics of some of them, as in testing the residues of malt liquors for color reactions of added colors and extracting them with solvents it would be necessary to take into consideration the influence these alkaloids would produce on such results.

**Absynthin.**—Easily soluble in alcohol and ether. Potassium hydroxid produces a brown color, and concentrated sulphuric acid, first a brown color, passing into a green blue.

**Aloin.**—Soluble in alcohol. Sulphuric acid (hydrous) first red, then orange. Potassium hydroxid, a purple red. Nitric acid produces chrysamic and picric acids.

**Onicin.**—Soluble in ethyl and methyl alcohol. Cold sulphuric acid gives a red solution, becoming violet on adding water and yellow on adding ammonia. Cold hydrochloric acid (concentrated) gives a green color.

**Daphnin.**—Soluble in alcohol. Alkalis give a red color, cold iron chlorid solution a blue color, which, when boiled, gives a yellow precipitate, and nitric acid a red color.

**Gentianin.**—Soluble in alcohol. Sulphuric acid (concentrated) gives yellow color. Nitric acid, dilute, a dark green, which, on addition of water, precipitates green dinitro-gentianin. Nitric acid (concentrated) produces trinitro gentianin (yellow).

**Quassinin.**—Yellow mass when heated. Precipitated by tannic acid. Sulphuric acid (concentrated) no color.

#### TESTS FOR COAL-TAR COLORS.

These will seldom be found, and, aside from fuchsin and picric acid (if added for bitters), need hardly be considered. By evaporating to small bulk and extracting with 80 per cent alcohol, the coal-tar colors may be examined for in the filtrate as given under wines.

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<sup>a</sup>J. Amer. Chem. Soc., 1899, 21, 356.

Picric acid (Fleck <sup>a</sup>).—Evaporate down about one-half liter of beer to consistency of sirup, mix the residue with ten times the amount of absolute alcohol, filter, wash, and evaporate the alcoholic solution to dryness, treat this residue with water as long as the water is colored, evaporate down the watery extract to dryness and extract with ether. The ether will contain picric acid in a state pure enough to weigh, if not absolutely pure. The ether may be driven off and the picric acid taken up by chloroform or benzol and crystallized from either solvent.

#### TESTS FOR VEGETABLE COLORS.

Caramel may be examined for, in general, as directed under wines. In addition, Schuster recommends agitating the beer with tannin solution. Pure beer will be decolorized, while the presence of caramel prevents decolorization. Griessmayer (1881) recommends adding to a beer highly colored twice its weight of ammonium sulphate crystals and three volumes of strong alcohol, and when agitated, if the beer be pure, complete decolorization will take place and a deposit will form, either brown or black if the coloration is due to malt. If colored with caramel the solution will remain brown and a gray or brownish deposit will be formed.

#### IV. Canned Vegetables.

Extract with acidified 80 per cent alcohol or extract with immiscible solvents and proceed as usual. Lendrich <sup>b</sup> states that it is not unusual for dried pease, either in the whole or split condition, to be artificially colored. They are generally treated with talc to give a polished surface. Colors employed are green or orange-yellows, and may be detected by shaking with 50 per cent alcohol and decanting the latter after about five minutes. Natural pease give a colorless solution. The following table <sup>c</sup> shows the behavior of the coloring matter from some vegetables extracted with 80 per cent alcohol:

*Behavior of coloring matters extracted from vegetables with 80 per cent alcohol.*

Vegetable.	Alcoholic extract.	Sulphuric acid, concentrated.	Sulphuric acid + water.	Hydrochloric acid, dilute.
Radish .....	Wine red .....	Brown-yellow .....	Orange .....	Orange.
Tomato .....	Brown-yellow .....	Red-brown .....	Brown .....	Lighter.
Pease .....	Yellow-green .....	Brown-violet .....	Yellowish .....	Yellow.
Carrot .....	Yellow .....	Brownish .....	Brownish .....	Straw yellow.
Red beet .....	Orange .....	Brown .....	Brown .....	No change.
Red onion .....	Blood red .....	Red-yellow .....	Red-brown precipitate.	Wine red.
Yellow onion .....	Yellowish .....	Red-yellow .....	Dirty yellow .....	No change.
Spinach .....	Dark green .....	Brown-yellow .....	Yellowish-brown precipitate.	No change.
Green pepper .....	Green .....	Pink-brown .....	Yellow-green .....	Yellowish.
Red pepper .....	Red-yellow .....	Pink-brown .....	Brown .....	Colorless.
Cucumber .....	Green .....	Pink-brown .....	Yellow-green .....	Yellow.

Vegetable.	Ammonium hydroxide, dilute.	Ammonium hydroxide, concentrated.	Lakes.
Radish .....	Blue-red fluorescence.	Green .....	
Tomato .....	Brighter .....	Brighter .....	Tin lake, light brown.
Pease .....	No change .....	No change .....	{ Aluminum lake, greenish. Tin lake, dirty brown.
Carrot .....	Green-yellow .....	Yellow .....	
Red beet .....	Dark orange .....	Green-yellow .....	
Red onion .....	Brown-yellow .....	Brown-yellow .....	{ Aluminum lake, golden yellow. Tin lake, yellow-brown.
Yellow onion .....	Green-yellow .....	Bright yellow .....	
Spinach .....	Yellow .....	Yellow .....	Lakes, green-yellow.
Green pepper .....	Green-yellow .....	Green-yellow .....	
Red pepper .....	Brighter .....	Brighter .....	Tin lake, light brown.
Cucumber .....	Brighter .....	Brighter .....	Aluminum lake, yellow.

<sup>a</sup> Correspondenz-BI. Verein. anal. Chem., 3, 77.

<sup>b</sup> Zts. Nahr. Genussm., 1904, 1.

<sup>c</sup> Prepared by the writer.

# V. Fruits, Fruit Juices (nonalcoholic), Preserves, Jam, Marmalade, etc.

Extract with 80 per cent acidified alcohol, or extract the coloring matter by means of immiscible solvents, and proceed as usual.

## RESULTS ON EXTRACTION OF FRUIT COLORS.

The extraction of fruit colors is shown in the following tables, the first of which was prepared by Truchon and Martin-Claude<sup>a</sup> and the second by Tolman.<sup>b</sup> The fresh fruit juice was very slightly acidified by hydrochloric acid before extraction. In no case in the dyeing test was there any danger of mistaking the vegetable color for one of coal-tar origin where the double-dyeing method was used.

### Extraction of fruit colors with amyl alcohol.

Fruit.	Coloration of acid solution. <sup>a</sup>		Coloration of ammoniacal solution.		Addition of a drop of H <sub>2</sub> SO <sub>4</sub> to dyed fabric.
	Juice.	Amyl-alcohol extract.	Juice.	Amyl-alcohol extract.	
Early cherries.....	Red .....	Yellow .....	Green .....	Uncolored....	Yellow. Yellow. Rose. Rose (tints silk a rose red).
Ripe cherries.....	Red .....	Uncolored..	Green .....	Uncolored....	
Early strawberries ..	Red .....	Rose.....	Green .....	Uncolored....	
Ripe strawberries ..	Red .....	Red .....	Green .....	Uncolored....	
Raspberries .....	Red .....	Red .....	Green .....	Uncolored....	Tints silk rose. Uncolored.
Red currants .....	Red .....	Uncolored..	Green .....	Uncolored....	
White currants.....	White .....	Uncolored..	Brown .....	Uncolored....	
Black currants.....	Dark red ..	Red .....	Deep green ..	Uncolored....	
Peaches .....	Yellow .....	Uncolored..	Brown .....	Yellow-red ..	
Pears .....	Yellow .....	Uncolored..	Brown .....	Yellow-red ..	
Quinces .....	Yellow .....	Uncolored..	Brown .....	Yellow-red ..	
Apples .....	Yellow .....	Uncolored..	Brown .....	Yellow-red ..	
Apricots .....	Yellow .....	Uncolored..	Brown .....	Yellow-red ..	
Green gage plums....	Yellow .....	Uncolored..	Brown .....	Yellow-red ..	

<sup>a</sup> Acidity of the juice.

### Extraction of fruit colors with amyl alcohol and with ether.

Fruit.	Color with ammonium hydroxid.	Color extracted by ether from acid solution.	Color extracted by amyl-alcohol from acid solution.	Dyeing tests on the juice.
Strawberry .....	Purple.....	None .....	Deep red .....	Color washed out.
Red raspberry .....	Purple.....	None .....	Deep red .....	All color does not wash out, but does not dye in the second acid bath.
Blackberry .....	Blue-purple ..	None .....	Very deep red.	Dyes purplish red in acid solution, but does not dye in the second acid bath.
Cherry .....	Purple.....	None .....	Red .....	Dyes purplish red in acid solution, but does not dye in the second acid bath.
Blackberry .....	Blue-purple ..	None .....	Red .....	Dyes purplish red in acid solution, but does not dye in the second acid bath.
Wild dewberry ....	Blue-purple ..	None .....	Red .....	Dyes purplish red in acid solution, but does not dye in the second acid bath.
Currant .....	Blue-purple ..	None .....	Red .....	Dyes purplish red in acid solution, but does not dye in the second acid bath.

<sup>a</sup> J. pharm. chim., 1901, 13, 174.

<sup>b</sup> U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, p. 111.

It will be seen from these two tables that amyl alcohol, as a rule, extracts fruit coloring matter from acid solution, while ether does not. Neither amyl alcohol nor ether extracted any color from the alkaline solution of the fruit juices.

Desmoulière<sup>a</sup> found that amyl alcohol extracts a yellow color from macerated apricots in the presence of acid or alkali. The yellow residue with sulphuric acid gives an indigo-blue color changing to brown violet. This reaction is identical with that for carotin. The color does not dye silk or wool.

#### DETECTION OF COCHINEAL.

Girard and Dupré, *Analyse des matières alimentaires*, etc., p. 580; U. S. Dept. Agr., Bureau of Chemistry, Bul. 65, p. 120.

### VI. Dairy Products, Fats, Oils, etc.

#### A. NATURAL AND ARTIFICIAL COLORS IN MILK.

In examining for the presence of added coloring matters it is well to consider first the nature of the natural coloring in milk and, consequently, in butter. The natural coloring matter of milk is "lacto chrome," which may be precipitated from milk whey by nitrate of mercury in bright red orange resin-like masses, softening at 100° C., freely soluble in water and hot alcohol, separating from the latter on cooling (Blyth). Cholesterin occurring in milk is soluble in hot alcohol, ether, bisulphid of carbon, and chloroform, and gives characteristic color reactions with certain reagents, as follows:

5 parts sulphuric acid and 1 part water, colored carmine red, then violet.—Moleschott's test.

1 part sulphuric acid and 1 part chloroform, colored blood red, violet, or purple.—Salkowsky's test.

The coloring matter of certain plants when eaten by cows imparts colors to milk, which, though not natural, may be present through natural means. Such are—

Marsh marigold and saffron, coloring yellow; rhubarb, opuntia, and madder, coloring red; buckwheat and forgetmenot, coloring blue. Certain bacteria in milk develop a blue color which turns cherry red on addition of caustic alkali, returning to blue on addition of acids (Blyth).

Among the artificial coloring matters which may be considered are the following:

*Vegetable colors.*—Saffron, rocou, alkanet, carrot juice (carotin), aspergeoire berries, marigold and carthamus flowers, chelidone juice, ranunculus, turmeric, annatto, etc.

*Coal-tar colors.*—Spirit yellow R, nitrosamine red, aurantia, phosphin, Martius yellow, picric acid, Mikado yellow, Mikado gold yellow, naphthol yellow S, naphthol yellow RS, Victoria yellow, coralline yellow, acid yellow, methyl orange, orange IV and similar azo colors, amidoazobenzol, anilin yellow (amidoazobenzol hydrochlorid), butter yellow (benzinazodimethyl anilin), diazobenzol, etc.

<sup>a</sup>Ann. chim. anal., 1902, 7, 323.

## B. BUTTER, FATS, AND OILS (FRESH).

Coal-tar colors will be present with few exceptions in the form of nonsulfonated bases and will be indicated by the following tests:

a. BUJARD AND BAIER TEST.<sup>a</sup>

Two to 3 grams of fat are dissolved in 5 cc of ether and shaken with 5 cc of concentrated hydrochloric acid (1.125). If coal-tar colors are present the solution will be colored decidedly red. Precaution: "Butter yellow" does not color hydrochloric acid (1.19), or does so only slightly. The acid solution may then be used for double dyeing a piece of wool, as described under "Wines," and the wool or the extracted dye further examined.

b. VANDRIKEN TEST.<sup>b</sup>

J. Vandriken states that pure butter is completely decolorized by amyl nitrite. Proceed as follows:

1. *Amyl nitrite* (acid).—To 2 cc of filtered butter add an equal volume of ether in a test tube. To this add 6 to 10 drops of amyl nitrite, and shake. Pure butter is decolorized at once. If unfiltered butter is used, more reagent must be added, and usually slightly warmed.

2. *Nitrous ether*.—To 2 cc of filtered butter add 2 cc of ether and 25 to 30 drops of nitrous ether and shake vigorously. The decolorization takes place more slowly than with amyl nitrite. Carotin is not decolorized; saffron, only slightly altered; curcuma, not decolorized; orlean, decolorized; annatto, not decolorized.

c. LEEDS METHOD.<sup>c</sup>

One hundred grams of butter should be dissolved in a tapped separator in 300 cc of petroleum ether of about 0.638 sp. gr. The water, etc., is tapped off, and the ethereal solution of the fat and coloring matters washed several times by agitation with water. The ethereal solution, poured off from the stearin which may have separated on standing, is then shaken with 50 cc of N/10 caustic potash solution, which is sufficient to effect the solution of all coloring matter capable of being dissolved by dilute alkali.<sup>d</sup> The alkaline solution is separated from the ethereal layer and very cautiously treated with dilute hydrochloric acid until faintly acid to litmus. The precipitate, consisting of coloring matter mixed with a little fatty acid, is filtered off and washed with cold water. If desired it may be weighed. The following table shows the reactions of the coloring matters, isolated in the above manner, when two or three drops of their alcoholic solutions are treated with an equal measure of the reagents (acids) mentioned.

<sup>a</sup> Hilfsbuch für Nahrungsmittelchemiker, 1900, 144.

<sup>b</sup> Ann. Pharm., 1901 (7), 110; Chem. Ztg. Rep., 1901, 106.

<sup>c</sup> Analyst, 12, 150; Allen, 3 (1), 355.

<sup>d</sup> A pale yellow color remaining in the petroleum ether is due only to the natural coloring matter of the butter.



*Reactions of coloring matters according to Leeds method.*

Coloring matter.	Reaction with—			
	Concentrated sulphuric acid.	Concentrated nitric acid.	Sulphuric and nitric acids.	Concentrated hydrochloric acid.
Annatto .....	Indigo blue, changing to violet.	Blue, becoming colorless on standing.	Blue, becoming colorless on standing.	No change, or merely dirty yellow or brown color.
Annatto, with decolorized butter.	Blue, becoming green and slowly changing to violet.	Blue, becoming green and colorless.	Decolorized .....	No change, or only dirty yellow.
Turmeric .....	Rose violet .....	Violet .....	Violet .....	Violet, becoming yellow on evaporation of acid.
Turmeric, with decolorized butter.	Violet, changing to purple.	Violet to red-violet.	Violet to red-violet.	Very fine violet.
Saffron .....	Violet to cobalt blue, changing to reddish brown.	Light blue, changing to light reddish brown.	Light blue, changing to light reddish brown.	Yellow, changing to dirty yellow.
Saffron, with decolorized butter.	Dark blue, changing to reddish brown.	Blue, changing to green and brown.	Blue, rapidly changing to purple.	Yellow, becoming dirty yellow.
Carrot .....	Amber brown ....	Decolorized .....	Decolorized with red fumes and odor of burnt sugar.	No change.
Carrot, with decolorized butter.	Reddish brown to purple.	Yellow and decolorized.	Yellow and decolorized.	Slightly brown.
Marigold .....	Dark olive green, not changing.	Blue, instantly changing to dirty yellow-green.	Green .....	Green, to yellow-green.
Safflower .....	Light brown .....	Partially decolorized.	Decolorized .....	No change.
Anilin yellow .....	Yellow .....	Yellow .....	Yellow .....	Yellow.
Martius yellow ...	Pale yellow .....	Yellow, red precipitate, magenta at margin.	Yellow .....	Yellow precipitate, which deflagrates when treated with ammonium hydroxid and heated.
Victoria yellow ...	Partially decolorized.	Partially decolorized.	Partially decolorized.	Yellow, color returns on neutralizing with ammonium hydroxid.

*d. SPECIAL TESTS (SAFFRON, TURMERIC, MARIGOLD, ANNATTO).**1. Martin test. <sup>a</sup>*

Add gradually 2 parts carbon bisulphid, with gentle agitation, to 15 parts of alcohol or wood spirits. Five grams of the butter to be tested, which need not be previously clarified, is shaken with 25 cc of this solution. On standing for a few minutes, the mixture separates into two layers, the lower of which is a solution of the fat in carbon disulphid while the upper alcoholic stratum will be yellow if any artificial coloring matter be present. If the butter be but slightly colored a larger amount should be employed. The alcoholic stratum will give a greenish coloration with nitric acid, and a red with hydrochloric acid and sugar if saffron be present. A brownish color with ammonia indicates turmeric, and a blackish coloration with silver nitrate marigold. If the alcoholic solution be evaporated to dryness, and the residue treated with concentrated sulphuric acid, annatto will be indicated by a greenish blue, and saffron by a blue, coloration. On adding a few drops of boric-acid solution and again evaporating turmeric will be indicated by a bright brownish-red coloration, changed to blue, green, or violet by caustic alkalies.

*2. Carotin test (Moore). <sup>b</sup>*

When a butter colored with carotin is dissolved in carbon disulphid and shaken with alcohol, as prescribed by Martin, the alcohol remains colorless, while the lower layer is deeply colored, but on adding a drop of a dilute solution of ferric chlorid and

<sup>a</sup> Analyst, 12, 70; Allen, 3, (1), 354.<sup>b</sup> Analyst, 12, 163.

again shaking a gradual change is observed, and the alcoholic layer becomes distinctly yellow and the bisulphid solution of the fats quite colorless, or retaining only the pale yellow color due to the natural coloring matter of the butter.

### 3. *Test for saffron, curcuma, carotin, rocou (Chevallier and Baudrimont).*<sup>a</sup>

Treat with warm alcohol and test extract with subacetate of lead, an orange color indicates the presence of saffron; treat with alkali and a brown color indicates curcuma, and a green color, carotin; treat with concentrated sulphuric acid and a red-brown color followed by blue indicates rocou.

### 4. *Test for egg yellow.*

Three hundred grams of fat are melted at 50° C., 150 cc of a 2 per cent solution of sodium chlorid added, and the mixture kept at 50° C. for two hours. The mixture is then well cooled and the aqueous solution separated and repeatedly passed through a filter until as clear as possible. A perfectly clear and colorless filtrate, however, indicates the absence of egg yolk. On adding an equal bulk of concentrated hydrochloric acid to a filtrate which is persistently turbid, a clear solution is obtained again, becoming turbid on heating. Should egg yolk be present a further test is to acidify 10 cc of the salt solution with 1 cc of a 1 per cent sulphuric-acid solution, heat to boiling for a short time, cool, and shake with 2 cc of ether. The latter dissolves the coloring matters of the egg yolk should any be present, and the ethereal layer is colored faint yellow. Consult an extended article on this subject by Dr. G. Fendler.<sup>b</sup>

## C. BUTTER, FATS, ETC. (RANCID).

If butter has become rancid the acid water from the petroleum ether extract as obtained when testing fresh butter should be examined for reduced coal-tar dyes by the method given below under milk (sour).

### D. MILK (FRESH).

#### a. LEACH'S METHOD.<sup>c</sup>

The author uses the generic name of "anilin orange" as applied to all the coal-tar dyes of the classes of diazo compounds of anilin, thus including single or mixed dyes under this head. About 150 cc of the milk are curdled by the aid of heat and acetic acid, preferably in a porcelain casserole over a Bunsen flame. By the aid of a stirring rod the curd can nearly always be gathered into one mass, which is much the easiest method of separation, the whey being simply poured off. If, however, the curd is too finely divided in the whey the separation is effected by straining through a sieve or colander. All of the annatto or of the anilin orange present in the milk treated would be found in the curd and part of the caramel. The curd pressed free from adhering liquid is picked apart, if necessary, and shaken with ether in a corked flask, in which it is allowed to soak for several hours or until all the fat has been extracted, and with it the annatto. If the milk is uncolored or has been colored with annatto, on pouring off the ether the curd should be left perfectly white. If, on the other hand, anilin orange or caramel has been used, after pouring off the ether the curd will be colored more or less deeply, depending on the amount of color employed. In other words, of the three colors, annatto, caramel, and anilin orange, the annatto only is extracted by the ether. If caramel has been used, the curd will have a brown color at this stage; if anilin orange, the color of the curd will be a more or less bright orange.

<sup>a</sup> Dict. des alterations et falsification des substances alimentaires, etc., 7th ed., p. 236.

<sup>b</sup> Zts. Nahr. Genussm., 1903, 971.

<sup>c</sup> J. Chem. Soc., 1900, 207.

The ether extract, containing the fat and the annatto, if present, is evaporated on the water bath, the residue is made alkaline with sodium hydroxid and poured upon a small, wet filter, which will hold back the fat and, as the filtrate passes through, will allow the annatto, if present, to permeate the pores of the filter. On washing off the fat gently under the water tap all the annatto of the milk used for the test will be found to have been concentrated on the filter, giving it an orange color, tolerably permanent and varying in depth with the amount of annatto present. The confirmatory test for annatto with stannous chlorid may afterwards be applied to the colored filter, producing the characteristic pink color.

The fat-free curd, if colored after the ether has been poured off, is examined further for caramel or anilin orange by placing a portion of the curd in a test tube and shaking vigorously with concentrated hydrochloric acid. If the color is caramel, the acid solution of the colored curd will gradually turn a deep blue on shaking, as would also the white fat-free curd of an uncolored milk, the blue coloration being formed in a few minutes if the fat has been thoroughly extracted from the curd; indeed, it seems to be absolutely essential for the prompt formation of the blue color in the acid solution that the curd be free from fat. Gentle heat will hasten the reaction. It should be noted that it is only when the blue coloration of the acid occurs in connection with a colored curd that caramel is to be suspected, and if much caramel be present the coloration of the acid solution will be a brownish blue. If the above treatment indicates caramel, it would be well to confirm by any of the usual tests on a fresh sample of the milk. If the milk has been colored with anilin orange, the colored curd, on applying the strong hydrochloric acid in the test tube, will immediately turn pink. In the case of caramel, the color of the curd itself remains unchanged, the solution only turning blue, and that gradually; on the contrary with the anilin orange the curd itself takes the pink color the moment the acid touches it. If a large amount of the anilin orange has been used in the milk, the curd will sometimes show the pink coloration when hydrochloric acid is applied directly to it, before treatment with ether, but the color reaction with the fat-free curd is very delicate and unmistakable.

#### *Summary of procedure.*

Curdle 150 cc of milk in casserole with heat and acetic acid. Gather curd into one mass. Pour off whey, or strain if curd is finely divided. Macerate curd with ether in a corked flask. Pour off ether.

Ether extract:

Evaporate off ether; treat residue with sodium hydroxid and pour on wetted filter. After solution has passed through wash off fat and dry filter, which, if colored orange, indicates presence of annatto. (Confirm by stannous chlorid.)

Collected curd:

(1) If colorless, indicates presence of no foreign color other than in ether extract.

(2) If orange or brownish, indicates presence of anilin orange or caramel.

Shake curd in test tube with concentrated hydrochloric acid.

(a) If solution gradually turns blue, indicates caramel. (Confirm by testing for caramel in whey of original milk.)

(b) If orange curd immediately turns pink, indicates anilin orange.

To differentiate the azo dyes included under the term "anilin orange," dye a piece of wool in the acid solution, extract the dye from the wool with ammonium hydroxid, and apply the tests as indicated in the table on page 34, headed "Coal-tar colors." <sup>a</sup>

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<sup>a</sup> Note by the writer.

*b. CARAMEL TEST<sup>a</sup> (MODIFICATION BY BLYTH OF LEACH'S TEST<sup>b</sup>).*

Use a milk known to be free from caramel as a control. Take 50 cc of the suspected milk and the same quantity of the control, coagulate each by the addition of acetic acid, strain off the whey from the curd by means of a piece of fine muslin. Carefully compare the colors of the whey from both samples. Place the curds in two white porcelain basins and just cover them with strong hydrochloric acid. Compare the colors after they have stood several hours. Caramel will be indicated by a brownish-violet color; but the pure curd will also develop a similar color after standing for a long time, so that great care must be exercised in coming to a conclusion. The use of the control milk greatly increases the delicacy of the test.

*E. MILK (SOUR), BLYTH'S METHOD.<sup>c</sup>*

The color of the milk should be carefully noted, as some dyes, such as anilin yellow and acid yellow, impart a faint pink color to the curd of sour milk. Butter yellow, on the other hand, rises with the fat, which it at first colors yellow, but afterwards becomes colorless. Annatto imparts a characteristic color to the curd and, like saffron and turmeric, does not become colorless in decomposed milk. Caramel colors both the curd and the whey. If it be desired to make a comparison between the milk when fresh and after partial decomposition, two portions should be incubated, one containing sufficient formalin to prevent any decomposition.

The following general method will be found most convenient: Take 50 cc or more of the milk and render it just alkaline to delicate litmus paper, evaporate to a paste, and thoroughly extract the fat with ether. Although turmeric, annatto, and such dyes as anilin yellow are all somewhat soluble in ether from an alkaline solution, yet in the presence of casein such small quantities are dissolved that they may be disregarded. (Phosphin is much more soluble in ether and should be looked for both in the ether and alcohol extract.)

Evaporate the ethereal solution to dryness, shake up the fat with a small quantity of hot distilled water in a small separating funnel, separate the water from the fat, and evaporate to dryness on the water bath in a small flat porcelain dish; carefully note the color of the residue. (See following table.) Pure milk will give no colored residue. Next thoroughly exhaust the fat-free milk residue with absolute alcohol, pass the extract through a small filter, and evaporate to dryness in three or four small flat porcelain dishes; if un-reduced artificial coloring matter be present the residue will be colored orange, yellow, or brown. Wash one of the residues into a test tube with a small quantity of water made acid with sulphuric acid. The sulphonated azo dyes will be at once indicated by the color of the solution. Shake the solution with ether. This will divide the coloring matters into two groups as in the table; the natural coloring matters and the non-sulphonated acid coal-tar dyes—i. e., the dyes precipitated by Weingartner's tannin reagent—being soluble in ether, while the basic dyes and the sulphonated dyes are insoluble in ether. The ordinary tests may then be applied to the remaining portions of the dyes.

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<sup>a</sup> Analyst, 1902, p. 151.

<sup>b</sup> Blyth finds that caramel may be formed from the milk sugar if any evaporation process be used in testing for caramel.

<sup>c</sup> Analyst, 1902, p. 146.

## a. ALCOHOL EXTRACT, COLORED ORANGE, YELLOW, OR BROWN.

Take up a portion of the residue with dilute sulphuric acid and shake with ether.

## (1) Ether dissolves some of the coloring matter:

Natural coloring matter—

Annatto.

Turmeric.

Saffron.

Carotin.

Nonsulphonated acid coal-tar colors, such as—

Anilin yellow.

Butter yellow.

Victoria yellow.

Martius yellow.

## (2) Ether does not dissolve the coloring matter:

Basic coal-tar colors, such as—

Phosphin.

Sulphonated coal-tar colors, such as—

Acid yellow.

Methyl orange.

Orange IV.

## b. WATER EXTRACT FROM THE FAT.

Note the color and apply various reagents to the dry residue.

Color of residue.	Probable original coloring matter.	Add drop of ferric chlorid.	To the ferric chlorid add strong sulphuric acid.	Other reactions.
Brown.....	Acid yellow ..	Dark green...	Yellow, green on dilution.	To slightly acid solution of the coloring matter add a few drops of hydrogen sulphid solution, then ferric chlorid, heat—magenta color.
Brown.....	Butter yellow.	Dark - blue green. .	Yellow, green on dilution.	
Brown.....	Anilin yellow.	Yellow .....	Yellow .....	Strong sulphuric or hydrochloric acid gives delicate violet.
Yellow ....	Martius yellow.	Red .....	Yellow .....	Strong hydrochloric acid gives a beautiful rose-red color.
Yellow ....	Victoria yellow.	Red .....	Yellow .....	Same as Martius yellow.
Rose red...	Methyl orange.	Fugitive scarlet.	Yellow .....	Treat as with butter yellow; the solution becomes a beautiful blue.
Brown red.	Orange IV....	Green .....	Scarlet, green on dilution.	Treat as butter yellow; the solution becomes a dirty violet.
Yellow ....	Unreduced dyes, soluble in ether from alkaline solution.			

## F. CHEESE.

Extract the dried cheese with hot alcohol, evaporate extract, and test residue for acid coal-tar colors and vegetable colors soluble in alcohol. Extract the cheese residue with petroleum ether for nonsulphonated coal-tar colors and vegetable colors insoluble in alcohol, and proceed as with butter and milk.

*Coal-tar colors.*

Colors.	Color on wool.	Sulphuric acid concentrated.	Water added.	Other reactions.
Nitrosamin red ..				Dilute hydrochloric acid precipitates para-nitrophenyl-nitrosamin.
Spirit yellow R. ....		Brown .....	Red precipitate.	Hydrochloric acid, red crystals.
Aurantia .....	Orange .....	Yellow precipitate.	Yellow precipitate.	Hydrochloric acid, hexanitrodiphenylamin.
Phosphin .....	Unmordanted cotton, yellow.	Red yellow, green fluorescence.	Red yellow .....	
Picric acid .....	Greenish yellow			Melting point, 122.5°; boiled with potassium cyanid gives brown coloration.
Martius yellow...	Golden yellow..	Yellow .....	Yellow precipitate.	Hydrochloric acid precipitates dinitro-naphthol, melting point of 138°.
Mikado yellow...	Cotton, yellow to orange.	Blue .....	Brown precipitate.	Hydrochloric acid, dark-brown precipitate.
Mikado gold yellow 2G.	Cotton, yellow..	Red to orange.	Yellow brown..	Hydrochloric acid, brown to yellow soluble precipitate.
Naphthol yellow S.	Yellow .....	Yellow .....	No precipitate..	Hydrochloric acid, no precipitate.
Naphthol yellow RS.	Yellow .....	Pale yellow...	No precipitate..	Hydrochloric acid, clear yellow.
Victoria yellow ..	Orange .....	Light yellow ..	No precipitate..	Hydrochloric acid precipitates, white dinitrocresol.
Coralline yellow.		Yellow .....	Yellow precipitate.	
Acid yellow .....	Yellow .....	Brown yellow.	Orange .....	Hydrochloric acid, orange.
Diazo-benzene ..				With acids forms colorless salts, turning brown; explosive.
Amido-azo-benzene.		Yellow brown.	Decomposed....	Yellow crystals, melting point 127.5°.
Butter yellow...		Yellow .....	Red .....	Yellow precipitate, melting point 115°.
Anilin yellow....		Brown .....	Red .....	Boiled with water precipitates yellow base, melting point 127.5°.
Methyl orange...	Yellow .....	Brown .....	Magenta red ..	Hydrochloric acid, magenta red.
Orange IV .....	Yellow .....	Violet .....	Violet precipitate.	Hydrochloric acid, violet precipitate. Crystallizes from boiling water in orange spangles.

## VII. Flesh Foods.

## NORMAL AND ABNORMAL COLORS.

Among the artificial coloring matters which may be considered are:

*Vegetable colors.*—Carmine, cochineal, logwood, archil, caramel, burnt chicory, liquorice, elderberry juices, etc.

*Coal-tar colors.*—Fuchsin, magenta red, diamond red, safranin, fluoresceine, eosines, ponceaus, Bordeaux reds, picric acid, benzopurpurin, and various mixtures of several dyes.

Vegetable colors are rarely used for flesh foods (Spaeth).

The normal red color of flesh is due to the presence of several coloring matters. Hemoglobin is the dark-purple coloring matter of venous blood. Oxyhemoglobin is the bright-red coloring matter of arterial blood. Lipochrome is the rosy-red coloring matter present in the muscular tissue of fishes. Healthy oysters may exhibit a green color, due to a pigment termed marennin. Normal horseflesh may exhibit a play of iridescent color.

Various abnormal colors not due to added coloring matter may be:

*Yellow*, due to food or to biliary compounds in disease.

*Brown*, due to greenish-brown pigments.

*Dark purple*, due to the animal having suffered from acute fevers, rinderpest, or tuberculosis, or to insufficient bleeding after killing.

*Dark red*, due to drowning or to suffocation in smoke (carbon dioxid poisoning).

*Dark brown*, hunted or overdriven.

*Scarlet*, from carbon monoxid poisoning or arsenic poisoning (Walley).

*Diffused redness*, from being frozen or to blood poisoning.

*Iridescence*, from disease of the blood in animals other than the horse.

*Green or violet*, commencement of putrefaction or diffusion of vegetable coloring matter through the membranes of the stomach after death (Walley). In diseased oysters due to green leucocytes.

Various *chromogenic bacteria*<sup>a</sup> also produce bright red, blue, green, or violet colorations.

The artificial coal-tar<sup>b</sup> colors used in sausages and meats in general may be conveniently divided into the following classes:

1. Those which color the meat but not the fat. In this case the surface of the meat is coated mechanically with some of the color, while the fat remains perfectly white. These dyes are insoluble in petroleum ether and generally insoluble in ether.

2. Those which color the meat and fat uniformly red. These are only mechanically distributed and are not in solution, and by melting the mass the fat separates colorless. These are insoluble in petroleum ether and generally in ether.

3. Those which color the meat and fat a uniform red color, the color being in solution (soluble form). The separated fat from the melted mass remains red. These colors are in general soluble in ether and insoluble in petroleum ether.

Three methods<sup>c</sup> may be used to advantage in the examination of flesh foods, each one having its advantage, viz:

<sup>a</sup> Consult C. A. Mitchell, *Flesh Foods*, 1900, p. 270.

<sup>b</sup> Juckenack and Sendtner, *Zts. Nahr. Genussm.*, 1899, 181.

<sup>c</sup> See also Polenské—*Arb. Kaiserl. Gesund.*, 1900, 17, 568. Schweissing—*Pharm. Centraltb.*, 27, 441. Reinsch—*Zts. öffentl. Chem.*, 1900, 485. Weller and Riegel—*Forschungsb.*, 1897, 4, 204.

*BUJARD AND BAIER METHOD.<sup>a</sup>*

The finely divided material is extracted repeatedly with 80 per cent alcohol, and the extract diluted with twice the quantity of water. Allow to stand until cold and filter, several times if necessary, until filtrate is clear. Place on the white surface and observe whether the solution is colored; if this be the case, evaporate on water bath to about 20 cc; allow to cool and filter. Examine the filtrate for coal-tar colors by methods given under wines.

*KLINGER AND BUJARD METHOD,<sup>b</sup> MODIFIED BY BREMER.<sup>c</sup>*

Twenty grams of finely minced material are heated for several hours with two volumes of a mixture of equal parts of glycerin and water made faintly acid with tartaric acid. The yellow solution freed from fat is filtered and the carmine precipitated with alum and ammonia as a lake. On placing the test tube before the microscope, the absorption lines of carmine-lake, lying between B and D, may then be identified. Since the acid solution of the sausage-coloring matter is yellow, while carmine-lake gives a red solution with acids, the carmine may be present in the sausages in some form combined with the preservatives insoluble in alcohol. Weller and Riegel concluded that this method was only reliable when the coloring matter could be precipitated from its solution as a lake. Since many vegetable colors, which are soluble in water but insoluble in alcohol or amyl alcohol can not be precipitated as lakes, this method may often fail.

*SPAETH METHOD.<sup>d</sup>*

Heat the finely divided material for some hours on the water bath at 100° C. and then extract with ether. The fat-free substance is then warmed on the water bath with a 5 per cent solution of sodium salicylate for one hour. The solution is filtered and ammonia added to one portion; observe whether a lake separates. As ammonia may sometimes give red precipitates, consisting of calcium and magnesium phosphates and possibly aluminum hydroxid carrying down traces of anilin colors mechanically, the precipitate obtained, if any, must be further examined for carmine. Another portion of the filtrate is acidified with sulphuric acid and heated with wool free from fat and examined for coal-tar colors, as under wines. It is not necessary to remove the precipitated salicylic acid before dyeing the wool.

*MICROSCOPIC EXAMINATION (MARPMANN).<sup>e</sup>*

A section of the sausage or other meat, about 1 cm thick, is thoroughly moistened with 50 per cent alcohol and examined under the microscope. When only traces of coloring matter are present, the substance is dehydrated in xylol, which is expelled by means of carbon tetrachlorid, and the mass placed in cedar oil. As thus prepared it is transparent and coloring matters can readily be recognized. Fuchsin, magenta red, diamond red, carmine, logwood, and archil stain the cell substances, while acid anilin colors dye the liquid in the cell. In some instances (e. g., with safranin) the coloring matter must be concentrated and wool or animal tissue placed in the concentrated solution. The finely-divided substance is digested with

<sup>a</sup> Hilfsbuch für Nahrungsmittelchemiker, 1900, p. 163.

<sup>b</sup> Zts. angew. Chem., 1891, p. 515.

<sup>c</sup> Forschungsberichte, 1897, p. 45, 216; C. A. Mitchell, *Flesh Foods*, p. 143.

<sup>d</sup> Pharm. Centraltb., 1897, 38, 884; Zts. Nahr. Genussm., 1901, 1020.

<sup>e</sup> Zts. angew. Mikros., 1895, p. 12; C. A. Mitchell, *Flesh Foods*, p. 142.



50 per cent alcohol, the liquid (fat-free) evaporated to a few drops, and some undyed sausage placed in this solution. The muscular fibers and the fat cells are then stained deeply. The sausages should also be extracted with ammonia water, which is a better solvent than alcohol for many of the colors used in flesh dyes. Marpmann regards with suspicion all sausages which remain colored after being kept for two hours in 50 per cent alcohol, since normal flesh is decolorized under these conditions. The following table shows the behavior of different flesh proteids on treatment with certain anilin colors:

*Behavior of flesh proteids treated with anilin colors.*

Flesh proteids.	Corallin.	Eosin.	Phloxin.	Congo red.	Safranin.
Albumin .....	Bluish-rose .....	Raspberry red	Raspberry red	.....	Decolorized.
Myosin .....	.....	Raspberry red	Raspberry red	.....	
Peptone .....	Orange-yellow, afterwards de- colorized.	.....	.....	Orange pre- cipitate.	
Nucleo-albumen ..	.....	Orange .....	.....	.....	Yellow. Yellow.
Syntonin .....	Reddish .....	.....	.....	Brown .....	
Alkaline albu- minate.	.....	Violet-rose ..	Reddish .....	Rose .....	
Fibrin .....	Red .....	Rose .....	Rose .....	Red .....	Yellow-red.

### VIII. Coffee, Tea, Cocoa, Spices, etc.

#### COLORING MATTERS CONSIDERED.

Turmeric, caramel, chicory, roasted cereals, azo dyes, indigo, catechu, campechy wood, humus, kino, graphite, mineral pigments.

#### FACINGS.<sup>a</sup>

Unroasted coffee beans contain viridic acid, which is soluble in sulphuric acid with a crimson color turning bright green on addition of alkalis. Inferior or damaged coffees are not infrequently treated by some process for improving their appearance and giving them the appearance of superior grades. For this purpose mineral pigments may be used for facing or coloring and azo dyes for brightening. The natural coloring matter of tea is extracted from the dry leaves by hot alcohol, giving a yellowish-green solution, turning bright yellow on adding ammonia. Sulphuric acid (conc.) on the color gives a bright green, remaining green on addition of water. The artificial colorings of tea will be found usually in the form of facings. They may be detected by the microscope by examining a portion of the leaf, when the coloring matter appears as small dots, or by chemical means.

#### AZO DYES.

Treat with hot strong alcohol, evaporate to dryness, take up with warm water and filter, or if necessary separate the fat or oil from the water solution by agitation with a suitable solvent. Examine the water solution for coal-tar colors, as under wines.

#### INDIGO.

Under the microscope indigo appears of a greenish blue. Its color is not discharged by sodium hydroxid, a distinction from Prussian blue. Indigo forms a deep blue solution with sulphuric acid. Hyposulphite of soda will dissolve indigo, reducing it at the same time. This solution may be used to dip a piece of wool in, which on exposure to the air will turn blue if indigo is present.

<sup>a</sup>U. S. Dept. Agr., Bureau of Chemistry, Bul. 13, Part 7, Tea, coffee, and cocoa preparations, pp. 880, 909.

*CATECHU (HAGER'S METHOD).<sup>a</sup>*

Small quantities of this substance can not be detected with certainty. Boil an extract of tea (1 gram per 100 cc of water) with an excess of litharge and filter; the filtrate should be clear. To a portion of the filtrate add a solution of silver nitrate. In the presence of catechu a yellow flocculent precipitate is formed, which rapidly becomes dark. Under the same conditions pure tea gives a slight grayish precipitate of metallic silver. The writer suggests agitating the tea extract with ether, evaporating the ether extract to dryness after shaking with bone char to decolorize, and testing the residue with concentrated sulphuric acid for the presence of catechin, which gives a deep purple coloration. Blyth <sup>b</sup> states that any amount present to the extent of 3 per cent or over is shown by precipitating an infusion of the tea with a slight excess of neutral lead acetate, filtering, and adding a little ferric chlorid (dilute). If catechu be present there is a bright-green color, and ultimately a precipitate of a grayish-green color. The same infusion filtered from the lead precipitate gives a copious precipitate with silver nitrate.

*CAMPECHY WOOD.<sup>c</sup>*

Eder exhausts 1 gram of tea with 100 cc of boiling water and adds chromate of potash, which gives a blackish-blue color if the wood is present.

*CHICORY.*

Chicory can be most readily and certainly identified in mixtures by means of the microscope. The microscopic appearances of coffee and chicory are shown in Bulletin 13.<sup>d</sup> Chemical methods for its detection are given by Wittstein,<sup>e</sup> Franz,<sup>f</sup> and Hiepe.<sup>g</sup>

*SANDERS WOOD IN COCOA.<sup>h</sup>*

Sometimes added for masking the addition of starch. Two to three grams are shaken with 10 cc of absolute alcohol. With pure cocoa the alcohol remains colorless or colored only a slight yellow, and gives a white precipitate with sodium hydroxid and no reaction with ferric chlorid. The filtered alcoholic extract from sanders wood or cocoa mixed with the latter is, on the other hand, colored, and gives with dilute sodium hydroxid an intense violet color. Should the wood have been previously exhausted this coloration is less pronounced. Ferric chlorid also yields a deep violet color with the unexhausted wood, but in the case of exhausted wood this reaction is only to be obtained by allowing a drop of the reagent to run on to the surface of the alcoholic extract. A violet ring is then formed, which disappears on shaking. Acetone may replace the alcohol.

*TURMERIC IN RHUBARB.<sup>i</sup>*

Anselmier shakes 0.1000 gram of the powder with 20 drops of olive oil for one minute. One drop of the mixture is then placed on white filter paper, when a characteristic yellow ring is formed should turmeric be present. The ring given by rhubarb can not be mistaken for the turmeric ring.

<sup>a</sup> Pharm. Central-Halle, 1879, 258.

<sup>b</sup> Blyth, Foods, 1896, p. 423.

<sup>c</sup> Bujard and Baier, Hilfsbuch, p. 225.

<sup>d</sup> U. S. Dept. Agr., Bureau of Chemistry, Bul. 13, Part 7, Tea, coffee, and cocoa preparations, plates 42, 43, and 45.

<sup>e</sup> Dingler's polytech. J., 211, 78.

<sup>f</sup> Arch. Pharm., (3) 8, 298.

<sup>g</sup> Moniteur scientifique, (3) 10, 1339.

<sup>h</sup> Zts. öffentl. Chem., 1902, 203. (R. & L.)

<sup>i</sup> Chem. Ztg. Rep., 1904, 80.

Bell<sup>a</sup> employs a reagent prepared by dissolving 1 gram of diphenylamin in 20 cc of 90 per cent alcohol and adding 25 cc pure sulphuric acid. A drop of this solution is placed on a microscopic slide; a small quantity of the powder under examination is spread over a cover glass and the latter placed on the slide, which is then examined. Turmeric develops purple-colored spots throughout the field of vision. This method is said to detect 1 part turmeric in 1,000 parts of mustard and 1 part in 200 of rhubarb.

#### PEPPER COLORS.

Sometimes colored with a preparation of sulpho-azo-benzol- $\beta$ -naphthol and barium sulphate (60 per cent). Such a colored powder gives with boiling water a beautiful red filtrate.<sup>b</sup> According to Mennechet<sup>c</sup> some peppers (those adulterated with the fruit of *Myrsine africana* L., and *Embelia ribes* Burm.) give a yellow extract when lixiviated with ether. If the ether extract be shaken with several volumes of water and rendered alkaline with ammonia a lilac-red color is produced, soluble in the water solution, but insoluble in the ether solution. If acidified the ether becomes colored again and the water solution decolorized.

#### IX. Starch Preparations (Pastry, Macaroni, Nudeln, etc.).

##### COLORS CONSIDERED.

Egg yellow, saffron, curcuma, orlean, picric acid, Victoria yellow, Martius yellow, naphthol yellow, etc.

##### METHOD FOR COAL-TAR COLORS (REICHELMANN AND LEUSCHER).<sup>d</sup>

Extract 50 grams of material on water bath with reflux condenser, and 75 cc of acetone for from forty-five minutes to one hour. Pour off the liquid into another flask and distill off acetone. Add 30 cc of water to residue in flask, cool and filter from the fat. The filtrate may be tested for coal-tar dyes by usual methods. Natural egg color will remain in the fat. In testing for tropæolin in pastry, Brebeck<sup>e</sup> has noticed that wheat, oatmeal, and other flours themselves contain a substance which gives the same violet coloration with sulphuric acid as does tropæolin and that it may be mistaken for the latter. Schmitz has also noticed that wheat gives a violet coloration, but only after some time; and Popp states that the color is due to the action of the acid on the oil contained in the flour. By removing the oil from the material by means of ether no reaction is obtained on flours.

#### X. Confectionery.

##### COLORS CONSIDERED.<sup>f</sup>

Cochineal and carmine lakes and alumnia lakes of vegetable colors. Carthamic acid, redwood dyes, cherry and beet juices, Chinese and spinach greens, indigo, litmus, archil blue, caramel, licorice, curcuma, kermes, alzarin and purpurin, and coal-tar colors in general. Alkaline buckthorn juice gives a green used for coloring pistache.

<sup>a</sup> Pharm. J., 1902, 551.

<sup>b</sup> Komm. des Arzneibuch, 2, 8.

<sup>c</sup> J. pharm. chim., 1901, [6] 14, 557.

<sup>d</sup> Zts. Nahr. Genussm., 1903, p. 175.

<sup>e</sup> Zts. öffentl. Chem., 1902, 397.

<sup>f</sup> Colors in Confectionery, the official circular of the National Confectioners' Association of the United States, February, 1899, contains a useful classified list of colors considered by them harmless or injurious. This list may also be found in Food Inspection and Analysis, 1904, by Leach.

## METHODS.

No unvarying method can be used for the examination of confectionery, owing to the wide range of material that enters into its composition, and much discretion must be used in making analyses in view of this fact. Portions may be advantageously isolated from each other mechanically, and after being roughly separated they are subjected to a preliminary treatment by agitating with warm water and allowed to stand for from 10 to 12 hours, when the water solution and insoluble residue are examined separately. According to whether the material is chiefly nitrogenous (as candied fruits, etc.) or of the carbohydrate class, a different line of examination should be adopted. In general, the following outline may be applied to the separated portions:

Digest with warm 20 per cent alcohol and filter.

<i>Residue.</i>		<i>Filtrate.</i>
Extract with immiscible solvents for colors not extracted by 20 per cent alcohol.		Examine as in wines by means of immiscible solvents and dyeing on wool.
Residue (if still colored): Treat with oxalic or tartaric acids and examine for color lakes.	Filtrate: Examine as usual.	
	After treatment with solvents examine for mineral pigments in the residues.	

Bujard and Baier<sup>a</sup> recommend extracting with alcohol, adding water and pouring 10 per cent hydrochloric acid over the residue and observing the degree of yellow color produced, an immediate yellow indicating picric acid and a yellow after a short time indicating dinitroresol. If treated with metallic zinc for from one to two hours, picric acid gives a blue color and dinitroresol a clear blood red.

<sup>a</sup>Hilfsbuch, p. 211.



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